

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

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The crystal structure of the title compound has been determined from single crystal X-ray diffractometer data collected at 168 K. $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$ crystallizes in space group $P2_1/c$ with $a=14.705(3)$, $b=15.240(4)$, $c=18.976(5)$ Å, $\beta=95.33(2)^\circ$ and $Z=4$. Block-diagonal least-squares refinement of the 469 structural parameters gave $R=0.060$ for 4435 observed independent reflections. The configuration of ligands about manganese is approximately octahedral with mean Mn–C, C–N and N–C distances of 1.901(4), 1.162(6) and 1.411(6) Å, respectively. The Mn–C–N and C–N–C linkages are almost linear.

Previous studies on hexacyano and hexakis(isocyanide) complexes of manganese and chromium (Ref. 1 and references cited therein) indicate that, provided sufficient d electrons are available, the π contribution to the metal-carbon bond increases with decreasing effective nuclear charge on the central metal atom. In hexakis(phenylisocyanide)-chromium(0),² the phenyl rings appear to stabilize the metal-ligand π system, enhancing back donation from metal to ligand. This is also in agreement with the interpretation³ of the electronic absorption spectra of some transition metal hexakis(phenylisocyanide) complexes. From comparative studies of alkyl and aryl isocyanide complexes it ought to be possible to ascertain the relative importance of this effect. Following the determination¹ of the structure of $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$, that of $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$ is now reported.

EXPERIMENTAL

Phenyl isocyanide, prepared according to Malatesta,⁴ and anhydrous manganese(II) iodide

were dissolved in absolute ethanol.⁵ $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$ and $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}$ were deposited within a few days from the ethanolic solution as yellowish-brown and bright yellow crystals, respectively. $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$ was recrystallized from ethanol. Despite numerous attempts to prepare high quality crystals of the compound, none superior to that used for the collection of data was obtained.

Intensities from a crystal $0.009 \times 0.011 \times 0.016$ cm were measured at 168 K with a Syntex $P2_1$ diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation and the ω -scan technique. Data were collected for $2\theta \leq 50^\circ$, $h \geq 0$ and $k \geq 0$, the ω scan speed being varied between 1 and 4°min^{-1} , according to the intensity of the reflection. Correction was made for Lorentz and polarization effects⁶ but not for absorption or extinction. Symmetry-related reflections were averaged giving 7598 unique reflections. Of these, 4435 for which $F_o^2 \geq 3\sigma(F_o^2)$ were used in the subsequent calculations. The unit cell parameters at 168 K and their standard deviations were determined by a least-squares procedure based on diffractometer setting angles for 13 reflections.

CRYSTAL DATA

Hexakis(phenylisocyanide)manganese(I) tri-iodide, $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$; $M_r=1054.4$; monoclinic, space group $P2_1/c$, $a=14.705(3)$, $b=15.240(4)$, $c=18.976(5)$ Å, $\beta=95.33(2)^\circ$, $Z=4$, $D_m=1.64 \text{ g cm}^{-3}$, $D_c=1.65 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha)=25.8 \text{ cm}^{-1}$. The compound crystallizes as yellowish-brown needles.

DETERMINATION OF THE STRUCTURE

The structure was solved from Patterson and successive electron density maps.⁶ Block-diagonal

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

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	-0.10073(7)	0.19540(7)	0.08367(6)	72.0(6)	72.3(6)	73.6(6)	18.5(10)	36.7(11)	28.7(10)
I(2)	0.09853(6)	0.18294(5)	0.09485(4)	70.1(5)	38.3(4)	41.0(4)	-5.6(8)	8.0(8)	5.8(7)
I(3)	0.29729(7)	0.16192(7)	0.10935(5)	63.3(5)	71.0(6)	64.9(6)	-39.5(10)	-6.4(9)	24.5(10)
Mn	0.3356(1)	0.0330(1)	0.4480(1)	23.5(7)	28.7(8)	21.5(7)	1.9(13)	5.3(12)	2.9(12)
C(1)	0.3761(7)	-0.0806(7)	0.4771(5)	23(5)	45(6)	26(5)	4(9)	8(8)	-15(9)
N(1)	0.3931(6)	-0.1529(6)	0.4934(4)	32(4)	30(4)	36(5)	3(8)	6(8)	-11(8)
C(11)	0.4071(7)	-0.2414(7)	0.5124(6)	41(6)	31(5)	32(6)	10(9)	19(10)	-4(9)
C(12)	0.4915(8)	-0.2784(7)	0.5082(6)	52(6)	36(6)	34(6)	25(11)	17(10)	-2(10)
C(13)	0.5032(9)	-0.3682(8)	0.5257(6)	66(8)	42(6)	32(6)	38(12)	10(12)	3(10)
C(14)	0.4299(9)	-0.4162(8)	0.5472(7)	56(7)	42(7)	62(8)	-8(12)	31(13)	8(12)
C(15)	0.3462(9)	-0.3772(9)	0.5507(8)	70(8)	47(7)	68(9)	-74(14)	25(14)	11(13)
C(16)	0.3318(8)	-0.2887(8)	0.5331(7)	45(7)	36(6)	59(8)	11(11)	3(12)	23(11)
C(2)	0.4385(6)	0.0566(6)	0.3970(5)	14(4)	29(5)	30(5)	-5(8)	3(8)	-2(8)
N(2)	0.4946(6)	0.0719(6)	0.3583(5)	32(4)	39(5)	36(5)	-15(8)	3(8)	7(8)
C(21)	0.5568(7)	0.0796(7)	0.3064(5)	39(5)	38(6)	27(5)	-11(10)	33(9)	1(9)
C(22)	0.5219(9)	0.0793(9)	0.2365(6)	65(8)	66(8)	30(6)	-21(14)	25(12)	16(12)
C(23)	0.5841(11)	0.0856(10)	0.1844(7)	89(10)	72(9)	35(7)	-45(16)	43(14)	-31(13)
C(24)	0.6774(9)	0.0912(9)	0.2054(7)	77(8)	52(8)	53(7)	-9(13)	81(15)	5(13)
C(25)	0.7118(9)	0.0923(9)	0.2760(8)	52(7)	52(8)	85(10)	-10(13)	65(16)	-5(15)
C(26)	0.6488(8)	0.0880(8)	0.3288(7)	34(6)	48(7)	63(8)	-13(11)	24(12)	3(12)
C(3)	0.2849(7)	0.1427(7)	0.4172(5)	33(5)	34(5)	27(5)	-14(9)	7(9)	-19(9)
N(3)	0.2518(6)	0.2097(6)	0.3976(5)	29(4)	40(5)	44(5)	1(8)	17(8)	-5(8)
C(31)	0.2059(7)	0.2827(7)	0.3677(6)	29(5)	28(5)	53(7)	21(9)	22(10)	24(10)
C(32)	0.1683(9)	0.2762(9)	0.2974(7)	48(7)	59(8)	50(8)	17(13)	-19(12)	23(13)
C(33)	0.1231(10)	0.3522(10)	0.2690(7)	70(8)	75(9)	51(8)	55(16)	19(14)	45(15)
C(34)	0.1162(10)	0.4262(9)	0.3095(8)	73(9)	47(7)	70(9)	26(14)	44(15)	24(14)
C(35)	0.1534(11)	0.4312(10)	0.3777(8)	80(9)	56(8)	71(10)	43(16)	36(16)	-1(15)
C(36)	0.1980(10)	0.3569(9)	0.4082(7)	73(8)	43(7)	48(7)	7(13)	23(13)	-7(12)
C(4)	0.2295(7)	0.0101(7)	0.4941(5)	33(5)	38(5)	17(5)	-3(9)	1(8)	3(8)
N(4)	0.1688(7)	-0.0079(6)	0.5254(4)	54(5)	37(5)	26(4)	9(9)	1(8)	21(8)
C(41)	0.0912(7)	-0.0256(8)	0.5631(5)	31(5)	54(7)	18(5)	3(10)	-11(8)	21(9)
C(42)	0.0571(8)	-0.1109(8)	0.5600(7)	41(6)	48(7)	67(8)	2(11)	31(13)	36(13)
C(43)	-0.0170(9)	-0.1293(9)	0.5992(8)	43(7)	59(8)	74(9)	1(12)	26(14)	35(14)
C(44)	-0.0549(8)	-0.0621(9)	0.6385(7)	30(6)	76(9)	47(7)	-11(12)	18(11)	17(13)
C(45)	-0.0190(8)	0.0211(9)	0.6377(6)	37(6)	77(9)	39(6)	-17(13)	11(11)	-19(12)
C(46)	0.0558(7)	0.0431(8)	0.5989(6)	27(5)	59(7)	43(6)	9(10)	19(10)	-19(11)
C(5)	0.2790(7)	-0.0171(7)	0.3637(5)	36(5)	32(5)	28(5)	15(9)	10(9)	2(9)
N(5)	0.2449(6)	-0.0506(6)	0.3130(5)	34(5)	40(5)	35(5)	10(8)	7(8)	-10(8)
C(51)	0.1985(7)	-0.0879(8)	0.2517(5)	31(5)	49(7)	26(5)	-2(10)	8(9)	-15(10)
C(52)	0.1732(9)	-0.0347(8)	0.1933(6)	71(8)	47(7)	25(6)	1(13)	11(11)	4(10)
C(53)	0.1248(10)	-0.0718(9)	0.1359(7)	76(9)	56(8)	41(7)	-12(14)	-13(13)	15(12)
C(54)	0.1029(10)	-0.1593(9)	0.1340(8)	59(8)	56(8)	60(9)	6(13)	-6(14)	-7(14)
C(55)	0.1288(10)	-0.2119(9)	0.1924(8)	70(9)	46(7)	62(9)	-4(14)	-33(15)	11(13)
C(56)	0.1777(9)	-0.1755(8)	0.2524(7)	63(8)	39(6)	42(7)	-8(12)	-16(12)	8(11)
C(6)	0.3879(7)	0.0826(7)	0.5358(6)	28(5)	32(5)	35(6)	21(9)	10(9)	1(9)
N(6)	0.4132(6)	0.1086(6)	0.5905(4)	34(4)	33(4)	24(4)	6(8)	10(7)	8(7)
C(61)	0.4425(8)	0.1373(6)	0.6597(5)	51(6)	17(5)	31(5)	15(9)	17(10)	-1(8)
C(62)	0.5310(8)	0.1650(8)	0.6756(6)	43(6)	48(7)	32(6)	-38(11)	-9(10)	-17(10)
C(63)	0.5593(9)	0.1949(9)	0.7441(7)	52(7)	56(8)	50(7)	5(13)	20(12)	-15(12)
C(64)	0.4988(9)	0.1927(8)	0.7951(6)	66(8)	39(6)	31(6)	-5(12)	13(11)	-16(10)
C(65)	0.4113(9)	0.1641(9)	0.7795(6)	73(8)	68(8)	25(6)	36(14)	43(12)	11(11)
C(66)	0.3780(9)	0.1361(9)	0.7099(6)	57(7)	62(8)	33(6)	8(13)	29(12)	-9(12)

least-squares refinement⁶ of the positional and anisotropic thermal parameters and a scale factor yielded $R=0.060$ for 469 parameters (4435 reflections); when the 3163 unobserved reflections were included $R=0.120$. The F_o values were weighted according to $w=(a+F_o+cF_o^2)^{-1}$ with $a=50.0$ and $c=0.0005$. The scattering factors were those of Doyle and Turner⁸ 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 $1.4 \text{ e } \text{\AA}^{-3}$. No attempt was made to locate the hydrogen atoms.

DISCUSSION

Stereoscopic projections⁶ of the complex ion and the unit cell are shown in Figs. 1–2. Bond distances and angles⁶ within the $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]^+$ ion are given in Tables 2–3. The manganese atom is octahedrally coordinated by the six phenyl isocyanide ligands at a mean Mn–C distance of

1.901(4) Å. The mean C–N and N–C distances are 1.162(6) and 1.411(6) Å, respectively, and the Mn–C–N and C–N–C linkages are almost linear (mean Mn–C–N $175.2(4)^\circ$, mean C–N–C $175.1(4)^\circ$). The geometry of the phenyl rings is normal, the maximum deviation of a carbon atom from the best plane through such a ring being 0.017 Å and the mean deviation 0.006 Å.

The short Mn(I)–C distance and relatively long C–N distance in $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$ is consistent with previous observations for cyanide and isocyanide complexes indicating (see Ref. 1) an increase in the metal $\rightarrow\pi^*$ (ligand) transfer with decreasing effective nuclear charge on the metal atom.

The Mn–C and N–C(R) distances in $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$ are shorter than those in $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$ (Table 4) indicating, moreover, that the π contribution to the Mn–C bond is enhanced by the presence of the phenyl rings. This effect appears to be even more pronounced in $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]$, judging by the short N–C(R) distance in this compound (Table 4).

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

Mn–C(1)	1.896(11)	C(1)–N(1)	1.165(14)
Mn–C(2)	1.905(9)	C(2)–N(2)	1.178(13)
Mn–C(3)	1.900(11)	C(3)–N(3)	1.176(14)
Mn–C(4)	1.891(10)	C(4)–N(4)	1.149(14)
Mn–C(5)	1.893(10)	C(5)–N(5)	1.161(13)
Mn–C(6)	1.923(10)	C(6)–N(6)	1.142(13)
N(1)–C(11)	1.406(13)	N(4)–C(41)	1.428(14)
C(11)–C(12)	1.373(16)	C(41)–C(42)	1.393(17)
C(12)–C(13)	1.414(16)	C(42)–C(43)	1.403(19)
C(13)–C(14)	1.395(18)	C(43)–C(44)	1.411(19)
C(14)–C(15)	1.374(19)	C(44)–C(45)	1.375(20)
C(15)–C(16)	1.401(18)	C(45)–C(46)	1.418(17)
C(16)–C(11)	1.408(16)	C(46)–C(41)	1.377(16)
N(2)–C(21)	1.410(14)	N(5)–C(51)	1.413(14)
C(21)–C(22)	1.377(16)	C(51)–C(52)	1.395(16)
C(22)–C(23)	1.411(19)	C(52)–C(53)	1.367(18)
C(23)–C(24)	1.396(21)	C(53)–C(54)	1.371(20)
C(24)–C(25)	1.389(21)	C(54)–C(55)	1.391(20)
C(25)–C(26)	1.427(19)	C(55)–C(56)	1.402(19)
C(26)–C(21)	1.386(16)	C(56)–C(51)	1.370(17)
N(3)–C(31)	1.394(14)	N(6)–C(61)	1.413(13)
C(31)–C(32)	1.400(18)	C(61)–C(62)	1.374(16)
C(32)–C(33)	1.418(20)	C(62)–C(63)	1.404(17)
C(33)–C(34)	1.374(21)	C(63)–C(64)	1.374(18)
C(34)–C(35)	1.360(22)	C(64)–C(65)	1.366(19)
C(35)–C(36)	1.407(20)	C(65)–C(66)	1.430(17)
C(36)–C(31)	1.378(17)	C(66)–C(61)	1.406(16)

Table 3. Angles (°) within the $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]^+$ ion. Estimated standard deviations are given in parentheses.

Mn–C(1)–N(1)	174(1)	C(1)–N(1)–C(11)	176(1)
Mn–C(2)–N(2)	172(1)	C(2)–N(2)–C(21)	172(1)
Mn–C(3)–N(3)	179(1)	C(3)–N(3)–C(31)	173(1)
Mn–C(4)–N(4)	175(1)	C(4)–N(4)–C(41)	177(1)
Mn–C(5)–N(5)	178(1)	C(5)–N(5)–C(51)	176(1)
Mn–C(6)–N(6)	174(1)	C(6)–N(6)–C(61)	177(1)
N(1)–C(11)–C(12)	119(1)	N(4)–C(41)–C(42)	117(1)
N(1)–C(11)–C(16)	118(1)	N(4)–C(41)–C(46)	117(1)
C(12)–C(11)–C(16)	123(1)	C(42)–C(41)–C(46)	125(1)
C(11)–C(12)–C(13)	118(1)	C(41)–C(42)–C(43)	117(1)
C(12)–C(13)–C(14)	120(1)	C(42)–C(43)–C(44)	120(1)
C(13)–C(14)–C(15)	121(1)	C(43)–C(44)–C(45)	119(1)
C(14)–C(15)–C(16)	121(1)	C(44)–C(45)–C(46)	123(1)
C(15)–C(16)–C(11)	117(1)	C(45)–C(46)–C(41)	115(1)
N(2)–C(21)–C(22)	118(1)	N(5)–C(51)–C(52)	120(1)
N(2)–C(21)–C(26)	118(1)	N(5)–C(51)–C(56)	118(1)
C(22)–C(21)–C(26)	124(1)	C(52)–C(51)–C(56)	122(1)
C(21)–C(22)–C(23)	118(1)	C(51)–C(52)–C(53)	118(1)
C(22)–C(23)–C(24)	119(1)	C(52)–C(53)–C(54)	122(1)
C(23)–C(24)–C(25)	122(1)	C(53)–C(54)–C(55)	120(1)
C(24)–C(25)–C(26)	118(1)	C(54)–C(55)–C(56)	120(1)
C(25)–C(26)–C(21)	118(1)	C(55)–C(56)–C(51)	118(1)
N(3)–C(31)–C(32)	118(1)	N(6)–C(61)–C(62)	120(1)
N(3)–C(31)–C(36)	119(1)	N(6)–C(61)–C(66)	117(1)
C(32)–C(31)–C(36)	123(1)	C(62)–C(61)–C(66)	123(1)
C(31)–C(32)–C(33)	116(1)	C(61)–C(62)–C(63)	120(1)
C(32)–C(33)–C(34)	121(1)	C(62)–C(63)–C(64)	119(1)
C(33)–C(34)–C(35)	122(1)	C(63)–C(64)–C(65)	121(1)
C(34)–C(35)–C(36)	119(1)	C(64)–C(65)–C(66)	122(1)
C(35)–C(36)–C(31)	119(1)	C(65)–C(66)–C(61)	115(1)
C(1)–Mn–C(2)	94.4(4)	C(2)–Mn–C(6)	95.3(4)
C(1)–Mn–C(3)	175.1(4)	C(3)–Mn–C(4)	89.3(4)
C(1)–Mn–C(4)	87.0(4)	C(3)–Mn–C(5)	88.0(4)
C(1)–Mn–C(5)	88.8(4)	C(3)–Mn–C(6)	92.0(4)
C(1)–Mn–C(6)	91.0(4)	C(4)–Mn–C(5)	90.0(4)
C(2)–Mn–C(3)	89.1(4)	C(4)–Mn–C(6)	87.3(4)
C(2)–Mn–C(4)	177.0(4)	C(5)–Mn–C(6)	177.3(4)
C(2)–Mn–C(5)	87.4(4)		

Table 4. Mean M–C, C–N and N–C bond lengths in hexakis(isocyanide) complexes of manganese and chromium.

Compound	Formal oxid. state of M	Formal ground state configuration	Mean M–C (Å)	Mean C–N (Å)	Mean N–C(R) (Å)	Ref.
$[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$	I	d^6	1.901(4)	1.162(6)	1.411(6)	present work
$[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$	I	d^6	1.924(3)	1.162(3)	1.447(4)	1
$[\text{Cr}(\text{CNC}_6\text{H}_5)_6]$	0	d^6	1.938(3)	1.176(4)	1.388(4)	2

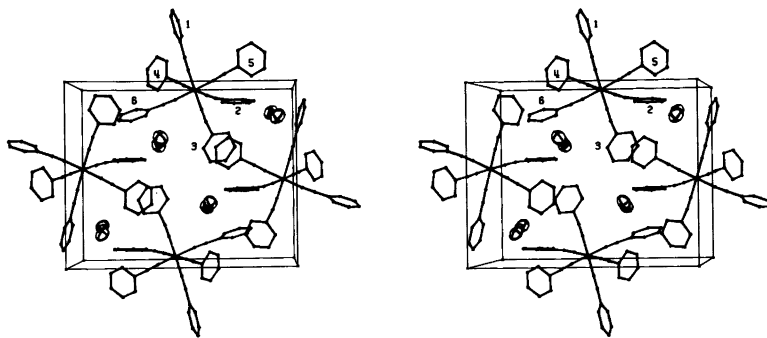


Fig. 1. Stereoscopic projection of the unit cell, perpendicular to the $b-c$ plane. a is away from the viewer, b is down the page, and c across from right to left. The ligands of the complex ion in (x, y, z) are numbered in accordance with Table 1.

In $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]$ phenyl rings *trans* to one another lie in the same plane.² Each such pair of rings is approximately perpendicular to one of the two planes through four cyanide ligands including both those bonded to the rings, and approximately contained in the other. This configuration would appear to be optimum for interaction between the $d-\pi^*$ (CN) system and the π systems (π^*, π_b) of the aromatic rings. Each of the three planes through the metal atom and four cyanide ligands contains a t_{2g} orbital on the metal atom and a $\pi^*(\text{CN})$ orbital on each of the four ligands. For interaction between the π orbitals of the aromatic groups of the four ligands with this system, the planes of the phenyl rings should be at 90° to the plane containing the cyanide groups. A configuration in which the planes of a pair of *trans* ligands are orientated perpendicular to the plane through the cyanide groups, while

the rings of the remaining pair are contained in the latter plane, ought therefore to be optimum for $d_\pi-\pi^*$ (CNC_6H_5) interaction with respect to all three t_{2g} orbitals.

As is seen from Fig. 1 and Table 5, the planes of mutually *trans* phenyl rings in $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$ are approximately perpendicular to one another. The orientation of the phenyl rings with respect to the relevant plane through four cyanide groups, each of which also contains the manganese atom, is, moreover, not as favourable for metal-cyanide-phenyl π bonding as in $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]$, there being large deviations from 90 and 0° . This is also reflected in the difference in the lengths of the $\text{N}-\text{C}(\text{R})$ bonds in the two complexes (Table 4).

A stronger π contribution to the $\text{M}-\text{C}$ bond in $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]$ is to be expected due to the lower effective nuclear charge on the metal atom. Metal-

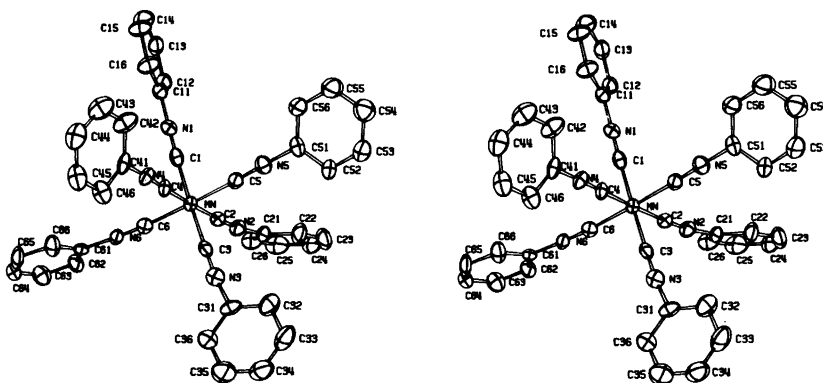


Fig. 2. Stereoscopic projection of the $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]^+$ ion orientated as that in (x, y, z) in Fig. 1. The thermal ellipsoids enclose 50 % probability.

Table 5. Angles ($^{\circ}$) between the three planes through four cyanide groups and the phenyl rings bonded to these groups; angles ($^{\circ}$) between the planes of mutually *trans* phenyl groups.

Plane A	Plane B	Dihedral angle
C(1), N(1)	C(11)–C(16)	18
C(2), N(2)	C(21)–C(26)	67
C(3), N(3)	C(31)–C(36)	104
C(4), N(4)	C(41)–C(46)	38
C(1), N(1)	C(11)–C(16)	78
C(3), N(3)	C(31)–C(36)	12
C(5), N(5)	C(51)–C(56)	22
C(6), N(6)	C(61)–C(66)	88
C(2), N(2)	C(21)–C(26)	156
C(4), N(4)	C(41)–C(46)	51
C(5), N(5)	C(51)–C(56)	115
C(6), N(6)	C(61)–C(66)	7
C(11)–C(16)	C(31)–C(36)	87
C(21)–C(26)	C(41)–C(46)	105
C(51)–C(56)	C(61)–C(66)	110

cyanide-phenyl π bonding in $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$ is, however, undoubtedly further reduced by interaction between the tri-iodide ion and the phenyl groups, causing the latter to twist from their ideal orientations. This is evident from Fig. 2 and from the short $\text{I}\cdots\text{C}$ contacts, of which there are several, the shortest, 3.76(1) and 3.80(1) Å, being considerably shorter than the shortest of those between the tri-iodide ion and the ethyl groups in $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$, *i.e.* 4.060(4)–4.098(3) Å.¹ In the molecular compound $[\text{Cr}(\text{CNC}_6\text{H}_5)_6]$, a configuration optimum for metal-phenyl isocyanide back donation is maintained in the solid state. A free $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]^+$ ion would presumably have the alternative, but equally favourable, configuration in which the phenyl rings of pair of *cis* ligands [(1)–(4), (2)–(6) and (3)–(5)] lie in the same plane, while mutually *trans* ligands are perpendicular to one another.

The tri-iodide ion is symmetrical [I(1)–I(2) 2.924(2), I(2)–I(3) 2.928(1) Å] and almost linear, I(1)–I(2)–I(3) 177.15(4) $^{\circ}$. The mean I–I distance, 2.926(1) Å, appears to be slightly shorter than that, 2.934(2) Å, in $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]\text{I}_3$ and closer to that suggested,⁹ 2.920 Å, for a free symmetrical tri-iodide ion. Interaction between the tri-iodide ion and the phenyl isocyanide ligands does thus not appear to affect the geometry of the tri-iodide ion. The closest

distance of approach between phenyl groups of adjacent $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]^+$ ions is 3.37(1) Å.

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