
5. Crystal Structure Determinations of the N,N'-substituted Nitrido Complexes of Manganese(V).

5.1. Introduction

In order to rationalise certain characteristics (like electron-donating properties, aromaticity and rigidity of bulky groups) of complexes with no or very little data available, it is helpful to do so in context of other well-known complexes. It is also important to rationalise the information obtained in such a way that all ligands employed and complexes studied are compared to one another on an identical scale.

Numerous crystal structure determinations of the substitution products as well as kinetic studies of the substitution reactions between the oxo- and nitridotetracyano complexes of molybdenum(IV), tungsten(IV), technetium(V) and rhenium(V) and monodentate ligands were undertaken in the past.^{1,2,3,4,5,6,7,8,9,10,11} However, only a few crystal structure determinations^{12,13,14} and kinetic studies^{15,16,17} were reported for the reactions between the oxotetracyano complexes of molybdenum(IV) and tungsten(IV) and bidentate ligands. No crystal structure determinations for the

¹ Leipoldt, J.G.; Basson, S.S.; Roodt, A.; Purcell, W., *Polyhedron*, **1992**, *11*, 2277.

² Leipoldt, J.G.; Basson, S.S.; Roodt, A., *Advances in Inorganic Chemistry*, ed. Sykes A.G., **1993**, *40*, 241.

³ Roodt, A.; Abou-Hamdan, A.; Engelbrecht, H.P.; Merbach, A.E., *Advances in Inorganic Chemistry*, ed. Sykes A.G., **2000**, *49*, 59.

⁴ Basson, S.S.; Leipoldt, J.G.; Potgieter, I.M.; Roodt, A., *Inorg. Chim. Acta*, **1985**, *103*, 121.

⁵ Leipoldt, J.G.; Basson, S.S.; Roodt, A.; Potgieter, I.M., *S. Afr. J. Chem.*, **1986**, *39*, 179.

⁶ Roodt, A.; Leipoldt, J.G.; Basson, S.S.; Potgieter, I.M., *Transition Met. Chem.*, **1990**, *15*, 439.

⁷ Purcell, W.; Roodt, A.; Basson, S.S.; Leipoldt, J.G., *Transition Met. Chem.*, **1989**, *14*, 369.

⁸ Purcell, W.; Potgieter, I.M.; Damoense, L.J.; Leipoldt, J.G., *Transition Met. Chem.*, **1991**, *16*, 473.

⁹ Purcell, W.; Damoense, L.J.; Leipoldt, J.G., *Inorg. Chim. Acta*, **1992**, *195*, 217.

¹⁰ Damoense, L.J.; Purcell, W.; Leipoldt, J.G., *Transition Met. Chem.*, **1994**, *19*, 619.

¹¹ Van der Westhuizen, H.J.; Basson, S.S.; Leipoldt, J.G.; Purcell, W., *Polyhedron*, **1994**, *13*, 717.

¹² Basson, S.S.; Leipoldt, J.G.; Potgieter, I.M., *Inorg. Chim. Acta*, **1984**, *87*, 71.

¹³ Szklarzewicz, J.; Samotus, A.; Alcock, N.W.; Moll, M., *J. Chem. Soc. Dalton Trans.*, **1990**, 2959.

¹⁴ Leipoldt, J.G.; Basson, S.S.; Roodt, A.; Potgieter, I.M., *Transition Met. Chem.*, **1986**, *11*, 323.

¹⁵ Leipoldt, J.G.; Basson, S.S.; Potgieter, I.M.; Roodt, A., *Inorg. Chem.*, **1987**, *26*, 57.

¹⁶ Samotus, A.; Kanas, A.; Glug, W.; Szklarzewicz, J., *Transition Met. Chem.*, **1991**, *16*, 614.

¹⁷ Roodt, A.; Basson, S.S.; Leipoldt, J.G., *Polyhedron*, **1994**, *13*, 599.

substitution products of the reactions between nitridotetracyano complexes of any of the above-mentioned metal centers and bidentate ligands are known up to date.

An investigation into the substitution reactions between the nitridotetracyano complexes of manganese(V) and bidentate ligands was undertaken during the course of this study. Suitable amine type ligands with different steric and electronic properties were chosen for this purpose. Thus, structural and electronic effects induced by changing stepwise from a non-rigid carbon backbone to a more rigid carbon backbone in these amine ligands were attempted. The stepwise functionalization of the bidentate ligands was investigated in order to determine the effect that a diverse substitution pattern of bidentate amine type ligands would have on the coordination mode, the bite angle of the bidentate ligands and the possible distortion of the coordination octahedron.

5.2. Experimental

The data collections for the X-ray structure determinations of these N,N'-substituted complexes of the nitridotetracyano complexes of manganese(V) were performed on a 1K Bruker SMART CCD area detector (University of the Witwatersrand) $\{(\text{Ph}_4\text{As})[\text{MnN}(\text{en})(\text{CN})_3]\}$ and an Oxford Diffraction Xcalibur 2 CCD (University of Natal; Pietermaritzburg Campus) $\{(\text{Ph}_4\text{P})[\text{MnN}(\text{bipy})(\text{CN})_3] \cdot 0.5(\text{bipy}) \cdot 2\text{H}_2\text{O}$ and $(\text{Ph}_4\text{P})[\text{MnN}(\text{phen})(\text{CN})_3]\}$. Graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at ambient temperature (293 K) was used for the determination of the crystal structure of $(\text{Ph}_4\text{As})[\text{MnN}(\text{en})(\text{CN})_3]$ and low temperature (220 K) was used for the determination of the crystal structures of $(\text{Ph}_4\text{P})[\text{MnN}(\text{bipy})(\text{CN})_3] \cdot 0.5(\text{bipy}) \cdot 2\text{H}_2\text{O}$ and $(\text{Ph}_4\text{P})[\text{MnN}(\text{phen})(\text{CN})_3]$. The densities of the crystals were determined by flotation in benzene/diiodomethane.

All the structures were solved with conventional Patterson and Fourier methods and refined through full-matrix least-squares calculations using SHELXL97¹⁸ series of

¹⁸ Sheldrick, G.M., SHELX-97, *Program for the refinement of crystal structures*, University of Göttingen, Germany, 1997.

5. STRUCTURES OF N,N'-SUBSTITUTED COMPLEXES

programmes, with $\Sigma(F_o/-F_c)^2$ being minimised. All non-hydrogen atoms were refined anisotropically, while the hydrogen atom positions were calculated as riding on the adjacent carbon atom (methylene C-H as 0.97 Å, methyl C-H = 0.96 Å, amine N-H = 0.89 Å and aromatic C-H = 0.96 Å). The hydrogen atoms of the water molecules of crystallization were determined geometrically from difference Fourier maps. The program Diamond¹⁹ was used to produce molecular diagrams of each of the respective complexes.

A summary of the general crystal data and refinement parameters for all the N,N'-substituted nitridotetracyano complexes of manganese(V) is provided in Table 5.1.



¹⁹ Brandenburg, K.; Diamond (Ver. 2.1e), Crystal Impact GbR, Bonn, Germany, **2001**.

Table 5.1: Crystallographic data for the different N,N'-substituted nitrido complexes of manganese(V).

Crystal data	Mnen ^a	Mnbipy ^b	Mnphen ^c
Empirical formula	C ₂₉ H ₂₈ N ₆ AsMn	C ₄₂ H ₃₆ N ₇ O ₂ P Mn	C ₃₉ H ₂₈ N ₆ PMn
Formula weight	590.43	756.69	666.58
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
a (Å)	13.443(1)	9.933(7)	16.137(6)
b (Å)	23.373(2)	12.608(6)	15.189(5)
c (Å)	11.128(1)	15.578(9)	14.817(5)
α (°)	90	75.75(5)	90
β (°)	126.645(1)	83.81(5)	114.09(3)
γ (°)	90	88.02(5)	90
Volume (Å ³)	2805.4(4)	1880(2)	3315(2)
Z	4	2	4
ρ _{exp} (g cm ⁻³)	1.40	1.32	1.32
ρ _{calc} (g cm ⁻³)	1.398	1.337	1.335
Crystal size (mm)	0.25 x 0.125 x 0.10	0.40 x 0.10 x 0.10	0.20 x 0.10 x 0.10
Absorption coefficient (mm ⁻¹)	1.699	0.440	0.484
F(000)	1208	786	1376
θ range (°)	1.74 to 26.00	4.13 to 29.00	4.23 to 30.00
Index ranges	-16 ≤ h ≤ 14 -28 ≤ k ≤ 28 -13 ≤ l ≤ 13	-13 ≤ h ≤ 13 -16 ≤ k ≤ 17 0 ≤ l ≤ 21	-20 ≤ h ≤ 22 -20 ≤ k ≤ 21 -20 ≤ l ≤ 20
Reflections collected / unique / observed	20651 / 5507 / 2531	9848 / 9848 / 3411	31657 / 9618 / 3240
R(int)	0.1149	0.0000	0.1469
Completeness to 2 theta (° ; %)	26.00, 100.0	29.00, 98.4	30.00, 99.4
T _{max} ; T _{min}	0.846; 0.779	0.957; 0.949	0.953; 0.944
Data / restraints / parameters	5507 / 0 / 334	9848 / 0 / 494	9618 / 0 / 424
Goodness-of-fit on F ²	0.835	0.752	0.998
Final R indices [I > 2σ(I)]	R ₁ = 0.0466 wR ₂ = 0.0943	R ₁ = 0.0524 wR ₂ = 0.0485	R ₁ = 0.0852 wR ₂ = 0.1323
R indices (all data)	R ₁ = 0.1282 wR ₂ = 0.1120	R ₁ = 0.1778 wR ₂ = 0.0699	R ₁ = 0.2898 wR ₂ = 0.2098
Largest diff. peak and hole (e.Å ⁻³)	0.404 and -0.583	0.723 and -0.507	1.561 and -0.875

^a Mnen = (Ph₄As)[MnN(en)(CN)₃]

^b Mnbipy = (Ph₄P)[MnN(bipy)(CN)₃]·0.5(bipy)·H₂O

^c Mnphen = (Ph₄P)[MnN(phen)(CN)₃]

5.3. (Ph₄As)[MnN(en)(CN)₃]

5.3.1. Introduction

The preparation of the (Ph₄As)[MnN(en)(CN)₃] complex is reported in § 3.3.11. A molecular diagram showing the numbering scheme of the anion is presented in Figure 5.1 and selected bond distances and angles are given in Table 5.2 with a discussion highlighting some of the important aspects of the [MnN(en)(CN)₃]⁻ anion presented thereafter. A comparison with other relevant structures is given in § 5.6. Supplementary data containing complete lists of atomic coordinates, anisotropic displacement parameters, bond distances and angles as well as hydrogen coordinates are given in § A.5 in Appendix A.

The (Ph₄As)[MnN(en)(CN)₃] compound crystallized in a monoclinic space group, *P*2₁/*c*, with four molecules per unit cell. The structure of this compound consists of discrete tetraphenylarsonium cations and [MnN(en)(CN)₃]⁻ anions. The geometry of the (Ph₄As)⁺ cation is tetrahedral with an average As-C bond distance of 1.915(5) Å. The C-As-C bond angles range from 106.8(2)° to 112.4(2)° and the geometries of the phenyl rings are within normal limits.^{20,21}

²⁰ Van der Westhuizen, H.J.; Basson, S.S.; Purcell, W., *Transition Met. Chem.*, **1994**, 19, 582.

²¹ Purcell W.; Potgieter I. M.; Damoense L. J.; Leipoldt J. G., *Transition Met. Chem.*, **1992**, 17, 387.

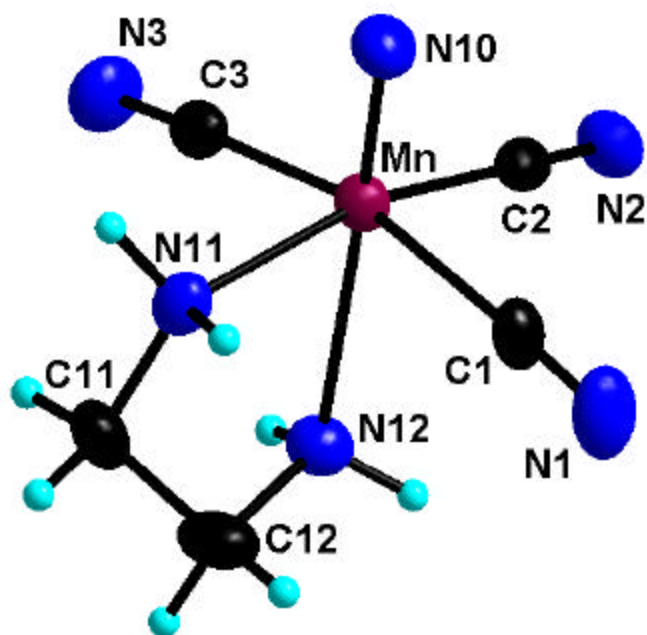


Figure 5.1: Molecular diagram showing the numbering scheme and displacement ellipsoids (30 % probability) of the $[\text{MnN}(\text{en})(\text{CN})_3]^-$ anion. The cation is omitted for clarity.

Table 5.2: Selected bond distances (Å) and angles (°) for the [MnN(en)(CN)₃]⁻ anion.

Bond distances (Å)			
Mn-N(10)	1.532(4)	Mn-C(2)	1.972(6)
Mn-C(3)	1.983(6)	Mn-C(1)	1.995(6)
Mn-N(11)	2.074(4)	Mn-N(12)	2.327(4)
C(1)-N(1)	1.147(6)	C(2)-N(2)	1.142(6)
C(3)-N(3)	1.147(6)	N(11)-C(11)	1.458(6)
C(11)-C(12)	1.482(7)	C(12)-N(12)	1.463(6)
Bond angles (°)			
N(10)-Mn-C(3)	98.4(2)	N(10)-Mn-C(2)	98.1(2)
N(10)-Mn-C(1)	97.7(2)	C(2)-Mn-C(3)	87.37(19)
C(3)-Mn-C(1)	163.9(2)	C(2)-Mn-C(1)	90.6(2)
C(2)-Mn-N(11)	162.81(18)	N(10)-Mn-N(11)	99.09(19)
C(1)-Mn-N(11)	88.11(18)	C(3)-Mn-N(11)	89.16(18)
C(2)-Mn-N(12)	85.40(17)	N(10)-Mn-N(12)	176.49(19)
C(1)-Mn-N(12)	81.62(18)	C(3)-Mn-N(12)	82.28(18)
N(1)-C(1)-Mn	177.9(5)	N(11)-Mn-N(12)	77.46(14)
N(3)-C(3)-Mn	176.9(5)	N(2)-C(2)-Mn	176.7(5)
N(11)-C(11)-C(12)	109.7(5)	C(11)-N(11)-Mn	113.5(3)
C(12)-N(12)-Mn	106.7(3)	N(12)-C(12)-C(11)	109.3(5)

5.3.2. Results and discussion

The manganese(V) ion in [MnN(en)(CN)₃]⁻ is octahedrally coordinated to a nitrido ligand, three carbon atoms of the cyano ligands and the two nitrogen atoms of the 1,2-diaminoethane (en) ligand. The Mn=N bond distance of 1.532(4) Å is of the expected magnitude. The Mn-C-N chains are nearly linear [average Mn-C-N bond angle = 177.2(5)°] and the average Mn-C bond distance of the *trans* orientated cyano ligands is 1.989(6) Å, comparable to the average bond distance of 1.990(6) Å in [MnN(CN)₅]³⁻²² for the four equatorially bonded cyano ligands. The Mn-C bond distance of 1.972(6) Å of the cyano ligand bonded *trans* to the nitrogen atom of the

²² Bendix, J.; Deeth, R.J.; Weyhemüller, T.; Bill, E.; Wieghardt, K., *Inorg. Chem.*, **2000**, 39, 930.

1,2-diaminoethane ligand in the equatorial plane is slightly shorter than the two *trans* bonded cyano ligands. The Mn-N(11) bond distance is longer than expected [2.074(4) Å].

The [MnN(en)(CN)₃]⁻ anion has a distorted octahedral geometry with the manganese(V) metal center displaced by 0.290(2) Å towards the nitrido ligand from the plane formed by the three carbon atoms of the cyano ligands and equatorially bonded nitrogen atom [N(11), Figure 5.1] of the 1,2-diaminoethane ligand. This displacement is also indicative of the large *trans* influence of the nitrido ligand on the ligand bonded *trans* towards it. The deviation of the bond angles between the two axial bonded atoms, the metal center and the equatorial atoms from the required 90° for the ideal octahedron also is an indication of this distortion. The N(10)-Mn-C bond angles [range from 97.7(2)° to 98.4(2)°] and the N(12)-Mn-C bond angles [range from 81.62(18)° to 85.40(17)°] are indications of the deviation from the expected angular geometry for the ideal octahedron. The small bite angle (N(11)-Mn-N(12) bond angle) for the 1,2-diaminoethane ligand, 77.46(14)°, coupled with the displacement of the manganese(V) atom out of the equatorial plane leads also to considerable distortion of the coordination octahedron. The lengthening of the Mn-N(12) bond distance [2.327(3) Å] compared to the Mn-N(11) bond distance [2.074(4) Å] is a direct consequence of the large *trans* influence of the terminal nitrido group on ligands bonded *trans* towards it. The bond distances and angles between the nitrogen atoms and the carbon atoms of the 1,2-diaminoethane ligand are (within experimental error) the same as were found for the [Rh(en)₃]³⁺ cation.²²

5.4. (Ph₄P)[MnN(bipy)(CN)₃]-0.5(bipy)-2H₂O

5.4.1. Introduction

The preparation of the (Ph₄P)[MnN(bipy)(CN)₃]-0.5(bipy)-2H₂O complex is reported in § 3.3.12. A molecular diagram showing the numbering scheme of the anion is presented in Figure 5.2 and selected bond distances and angles are given in Table 5.3 with a discussion highlighting some of the important aspects of the [MnN(bipy)(CN)₃]⁻ anion presented thereafter. A comparison with other relevant structures is given in § 5.6. Supplementary data containing complete lists of atomic coordinates, anisotropic displacement parameters, bond distances and angles as well as hydrogen coordinates are given in § A.6 in Appendix A.

The crystal structure determinations of (Ph₄P)[MnN(bipy)(CN)₃]-0.5(bipy)-2H₂O and (Ph₄As)[WO(bipy)(CN)₃]-0.5(bipy)-2H₂O¹³ have shown that these compounds are isomorphous. The (Ph₄P)[MnN(bipy)(CN)₃]-0.5(bipy)-2H₂O compound crystallized in a triclinic space group, $P\bar{1}$, with two molecules per unit cell. The structure consists of well separated tetraphenylphosphonium cations and [MnN(bipy)(CN)₃]⁻ anions as well as two water molecules of crystallization. The free 2,2'-bipyridine molecule of crystallization is situated with the bond between the two pyridine molecules on the center of symmetry and consequently, only half of the atoms of one of the pyridine rings of the 2,2'-bipyridine molecule were used in the refinement.

The phosphorus atom of the tetraphenylphosphonium cation is tetrahedrally bonded to the four phenyl rings with average P-C bond distances of 1792(3) Å and the C-P-C bond angles ranging from 108(6)° to 111.0(2)°. The bond distances and angles of the phenyl rings were within normal ranges for these types of moieties.^{8,23,24}

The free 2,2'-bipyridine is in the *trans* conformation with typical bond distances and angles found in other structure determinations containing free 2,2'-bipyridine

²³ Purcell, W.; Roodt, A.; Basson, S.S.; Leipoldt, J.G., *Transition Met. Chem.*, **1989**, *14*, 5.

²⁴ Bendix, J.; Meyer, K.; Weyhermüller, T.; Bill, E.; Metzler-Nolte, N.; Wieghardt, K., *Inorg. Chem.*, **1998**, *37*, 1767.

molecules.^{13,25}

The nitrogen atom [N(21)] of the free 2,2'-bipyridine molecule forms a hydrogen bond with an oxygen atom of one of the water molecules of crystallization [O(2W)•••N(21) = 2.983(5) Å]. A short intermolecular contact was also detected between the two oxygen atoms of the water molecules [O(2W)•••O(3W) = 2.78 Å]. The nitrogen atom [N(2)] of one of the cyano ligands also forms a hydrogen bond with one of the oxygen atoms of the water molecules [O(1W)•••N(2) = 2.944(5) Å].

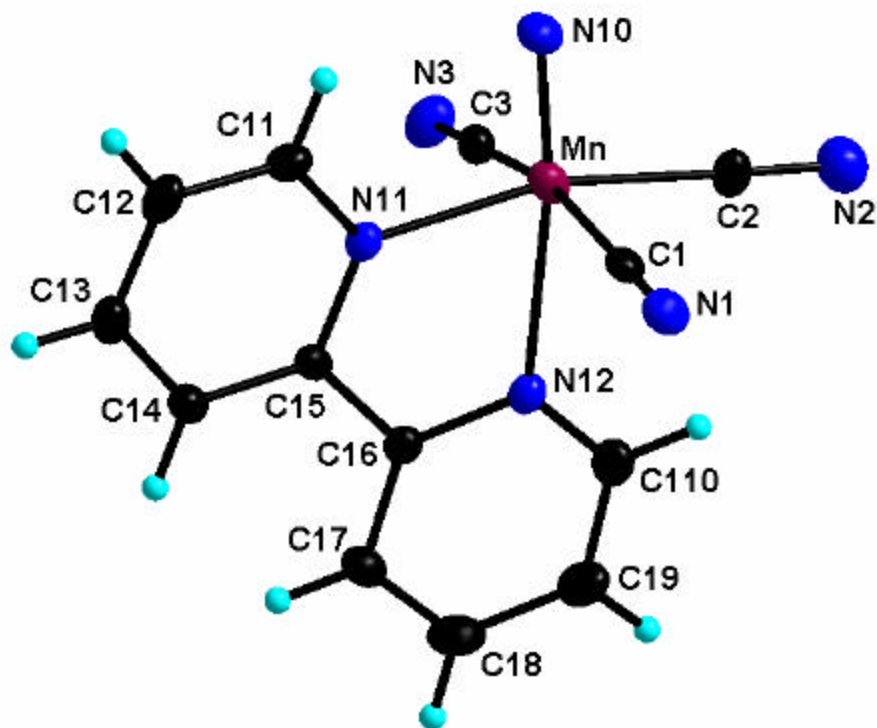


Figure 52: Molecular diagram showing the numbering scheme and displacement ellipsoids (30 % probability) of the $[\text{MnN}(\text{bipy})(\text{CN})_3]^-$ anion. The cation, free 2,2'-bipyridine ligand and solvent molecules are omitted for clarity.

²⁵ Durham, B.; Wilson, S.R.; Hodgson, D.J.; Meyer, T.J., *J. Am. Chem. Soc.*, **1980**, *102*, 600.

Table 5.3: Selected bond distances (Å) and angles (°) for the [MnN(bipy)(CN)₃]⁻ anion.

Bond distances (Å)			
Mn-N(10)	1.574(3)	Mn-C(2)	1.958(4)
Mn-C(3)	1.992(4)	Mn-C(1)	1.994(4)
Mn-N(11)	2.032(3)	Mn-N(12)	2.245(3)
C(1)-N(1)	1.145(4)	C(2)-N(2)	1.151(4)
C(3)-N(3)	1.153(4)	N(11)-C(11)	1.346(3)
N(11)-C(15)	1.359(3)	C(11)-C(12)	1.373(4)
C(12)-C(13)	1.373(4)	C(13)-C(14)	1.383(4)
C(14)-C(15)	1.378(4)	C(14)-H(14)	0.9300
C(15)-C(16)	1.465(4)	C(16)-N(12)	1.350(4)
C(16)-C(17)	1.401(4)	C(17)-C(18)	1.386(4)
C(18)-C(19)	1.374(4)	C(19)-C(110)	1.385(4)
C(110)-N(12)	1.324(4)		
Bond angles (°)			
N(10)-Mn-C(2)	97.35(15)	N(10)-Mn-C(3)	95.91(14)
C(2)-Mn-C(3)	89.76(15)	N(10)-Mn-C(1)	97.83(14)
C(2)-Mn-C(1)	88.22(14)	C(3)-Mn-C(1)	166.25(13)
N(10)-Mn-N(11)	96.94(13)	C(2)-Mn-N(11)	165.62(13)
C(3)-Mn-N(11)	90.34(12)	C(1)-Mn-N(11)	88.28(13)
N(10)-Mn-N(12)	171.25(12)	C(2)-Mn-N(12)	90.59(13)
C(3)-Mn-N(12)	80.39(13)	C(1)-Mn-N(12)	86.03(12)
N(11)-Mn-N(12)	75.25(11)	N(1)-C(1)-Mn	178.5(3)
N(2)-C(2)-Mn	175.6(4)	N(3)-C(3)-Mn	177.6(3)
C(11)-N(11)-C(15)	118.5(3)	C(11)-N(11)-Mn	121.0(2)
C(15)-N(11)-Mn	120.5(2)	N(11)-C(11)-C(12)	122.4(3)
C(13)-C(12)-C(11)	119.1(3)	C(12)-C(13)-C(14)	119.0(3)
C(15)-C(14)-C(13)	119.7(3)	N(11)-C(15)-C(14)	121.1(3)
N(11)-C(15)-C(16)	115.3(3)	C(14)-C(15)-C(16)	123.6(3)
N(12)-C(16)-C(17)	121.7(3)	N(12)-C(16)-C(15)	114.9(3)
C(17)-C(16)-C(15)	123.3(3)	C(18)-C(17)-C(16)	118.5(3)
C(19)-C(18)-C(17)	119.7(3)	C(18)-C(19)-C(110)	118.0(3)
N(12)-C(110)-C(19)	124.0(3)	C(110)-N(12)-C(16)	118.1(3)
C(110)-N(12)-Mn	127.8(2)	C(16)-N(12)-Mn	113.4(2)

5.4.2. Results and discussion

The manganese(V) metal atom is coordinated octahedrally to the nitrido ligand, three carbon atoms of the cyano ligands and the two nitrogen atoms of the 2,2'-bipyridine ligand. The Mn=N bond distance is 1.574(3) Å and is comparable to the similar bond distance found in the $[\text{MnN}(\text{CN})_5]^{3-}$ anion of 1.499(8) Å. The manganese(V) metal center is displaced by 0.243(2) Å from the equatorial plane formed by the three carbon atoms of the cyano ligands and the nitrogen atom [N(11)] of the 2,2'-bipyridine ligand. This distortion of the coordination polyhedron is also evident from the deviation from the expected rectangular values for the N(10)-Mn-C [range from 95.93(14)° to 97.84(14)°] and C-Mn-N(12) bond angles [range from 80.38(13)° to 90.62(13)°]. This, coupled with the small bite angle of 75.24(11)° of the chelating ligand (instead of the required 90° for an ideal octahedron) gives considerable distortion as evidenced in the less than 90° angles obtained for the bond angles between the equatorial ligands, the central metal atom and the ligand bonded *trans* the nitrido ligand. This is an indication of the large *trans* influence of the nitrido ligand towards the *trans* bonded ligand. The Mn-N(12) bond distance is 2.244(3) Å and can be compared to the Mn-N bond distance of 2.472(4) Å between the manganese(V) metal center and the nitrogen atom of the pyridine ligand in the $[\text{MnN}(\text{py})(\text{CN})_4]^{2-}$ anion.²²

The Mn-C bond distances of the bond between the metal center and the two cyano ligands that are bonded *trans* towards each other are 1.994(4) Å and 1.992(4) Å respectively and the Mn-C-N bond angles of these two ligands are nearly linear. However, the Mn-C(2) bond distance of 1.959(4) Å between the metal center and the carbon atom of the cyano ligand bonded *trans* towards the equatorial nitrogen atom of the 2,2'-bipyridine ligand is slightly shorter compared to the above-mentioned Mn-C bond distances. The Mn-N(11) bond distance is 2.032(3) Å. The shorter Mn-C(2) bond distance compared to the two *trans*-bonded cyano ligands can be explained in terms of the larger *trans*-influence of the cyano ligand on the ligands bonded *trans* to it.

The bonded 2,2'-bipyridine ligand is not abnormally distorted and its configuration is similar to those reported for the $[\text{WO}(\text{bipy})(\text{CN})_3]$ complex and other structures.^{13,25}

The C(15)-C(16) bond distance and the twist of $6.9(5)^\circ$ of the two pyridine groups about the C(15)-C(16) axis are very similar to the values reported in the tungsten(IV) complex [$7.8(5)^\circ$].

5.5. $(\text{Ph}_4\text{P})[\text{MnN}(\text{phen})(\text{CN})_3]$

5.5.1. Introduction

The preparation of the $(\text{Ph}_4\text{P})[\text{MnN}(\text{phen})(\text{CN})_3]$ complex is reported in § 3.3.13. A molecular diagram showing the numbering scheme of the anion is presented in Figure 5.3 and selected bond distances and angles are given in Table 5.4 with a discussion highlighting some of the important aspects of the $[\text{MnN}(\text{phen})(\text{CN})_4]^-$ anion presented thereafter. A comparison with other relevant structures is given in § 5.6. Supplementary data containing complete lists of atomic coordinates, anisotropic displacement parameters, bond distances and angles as well as hydrogen coordinates are given in § A.7 in Appendix A.

This compound crystallized in a monoclinic space group, $P2_1/c$, with four molecules per unit cell. The structure consists of discrete tetraphenylphosphonium cations and $[\text{MnN}(\text{phen})(\text{CN})_3]^-$ anions. Interestingly, no solvent molecules crystallized with the cation and anions in the unit cell. The bond distances and angles within the $(\text{Ph}_4\text{P})^+$ cation were normal and in good agreement with those found in previous reported structure determinations.^{23,24} The $(\text{Ph}_4\text{P})^+$ cation is tetrahedral with average P-C bond distances of $1.792(6)$ Å. The C-P-C bond angles range from $107.4(3)^\circ$ to $111.8(3)^\circ$ and the geometries of the phenyl rings were within normal limits.

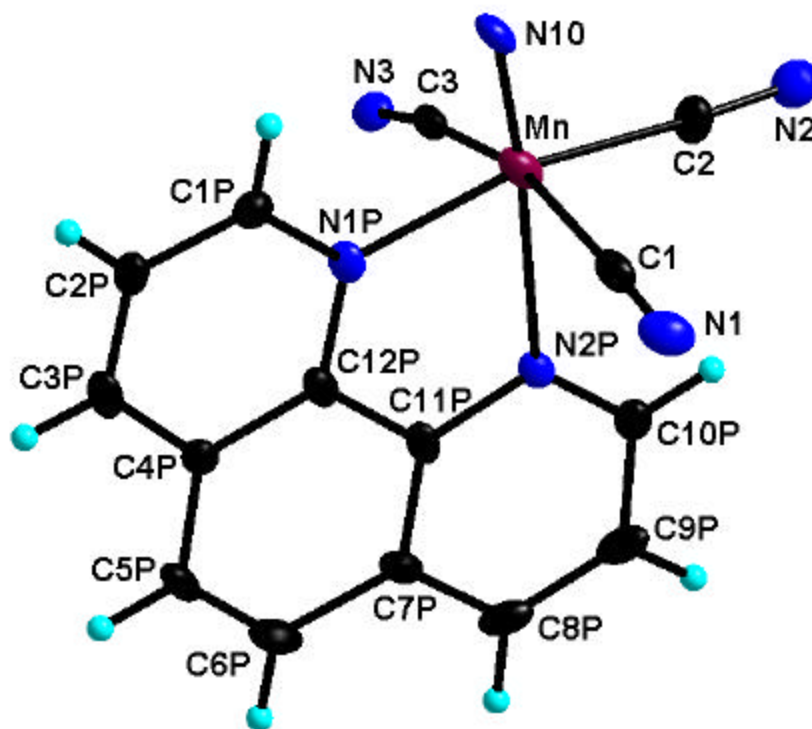


Figure 5.3: Molecular diagram showing the numbering scheme and displacement ellipsoids (30 % probability) of the $[\text{MnN}(\text{phen})(\text{CN})_3]^-$ anion. The cation is omitted for clarity.

5. STRUCTURES OF N,N'-SUBSTITUTED COMPLEXES

Table 5.4: Selected bond distances (Å) and angles (°) for the [MnN(phen)(CN)₃]⁻ anion.

Bond distances (Å)			
Mn-N(10)	1.568(5)	Mn-C(2)	1.939(6)
Mn-C(1)	2.012(7)	Mn-C(3)	2.013(6)
Mn-N(1P)	2.032(5)	Mn-N(2P)	2.268(5)
C(1)-N(1)	1.155(7)	C(2)-N(2)	1.173(7)
C(3)-N(3)	1.144(7)	N(1P)-C(1P)	1.322(7)
N(1P)-C(12P)	1.387(7)	C(1P)-C(2P)	1.394(8)
C(2P)-C(3P)	1.345(8)	C(3P)-C(4P)	1.411(8)
C(4P)-C(12P)	1.405(8)	C(4P)-C(5P)	1.418(8)
C(5P)-C(6P)	1.361(8)	C(6P)-C(7P)	1.444(8)
C(7P)-C(11P)	1.397(8)	C(7P)-C(8P)	1.405(8)
C(8P)-C(9P)	1.381(8)	C(9P)-C(10P)	1.408(8)
C(10P)-N(2P)	1.325(7)	C(11P)-N(2P)	1.350(7)
C(11P)-C(12P)	1.440(8)		
Bond angles (°)			
N(10)-Mn-C(2)	97.2(3)	N(10)-Mn-C(1)	98.4(2)
C(2)-Mn-C(1)	89.8(2)	N(10)-Mn-C(3)	99.9(2)
C(2)-Mn-C(3)	90.0(2)	C(1)-Mn-C(3)	161.5(2)
N(10)-Mn-N(1P)	97.6(2)	C(2)-Mn-N(1P)	165.2(2)
C(1)-Mn-N(1P)	89.1(2)	C(3)-Mn-N(1P)	86.4(2)
N(10)-Mn-N(2P)	174.0(2)	C(2)-Mn-N(2P)	88.8(2)
C(1)-Mn-N(2P)	81.4(2)	C(3)-Mn-N(2P)	80.2(2)
N(1P)-Mn-N(2P)	76.49(19)	N(1)-C(1)-Mn	177.9(6)
N(2)-C(2)-Mn	176.6(6)	N(3)-C(3)-Mn	171.9(5)
C(1P)-N(1P)-C(12P)	117.3(5)	C(1P)-N(1P)-Mn	124.6(4)
C(12P)-N(1P)-Mn	118.0(4)	N(1P)-C(1P)-C(2P)	123.1(6)
C(3P)-C(2P)-C(1P)	119.8(6)	C(2P)-C(3P)-C(4P)	120.6(6)
C(12P)-C(4P)-C(3P)	116.3(6)	C(12P)-C(4P)-C(5P)	118.9(6)
C(3P)-C(4P)-C(5P)	124.8(6)	C(6P)-C(5P)-C(4P)	121.8(6)
C(5P)-C(6P)-C(7P)	120.2(6)	C(11P)-C(7P)-C(8P)	117.1(6)
C(11P)-C(7P)-C(6P)	119.2(6)	C(8P)-C(7P)-C(6P)	123.6(6)
C(9P)-C(8P)-C(7P)	119.3(6)	C(8P)-C(9P)-C(10P)	118.9(6)
N(2P)-C(10P)-C(9P)	122.9(6)	N(2P)-C(11P)-C(7P)	124.0(5)
N(2P)-C(11P)-C(12P)	116.2(5)	C(7P)-C(11P)-C(12P)	119.7(5)
N(1P)-C(12P)-C(4P)	122.9(5)	N(1P)-C(12P)-C(11P)	117.0(5)
C(4P)-C(12P)-C(11P)	120.1(6)	C(10P)-N(2P)-C(11P)	117.8(5)
C(10P)-N(2P)-Mn	130.2(4)	C(11P)-N(2P)-Mn	111.9(4)

5.5.2. Results and discussion

The manganese(V) metal center is octahedrally coordinated to a nitrido ligand, the three carbon atoms of the three cyano ligands and the two nitrogen atoms of the 1,10-phenanthroline ligand. The Mn=N bond distance is 1.568(5) Å and this bond distance is comparatively short.^{22,24} The Mn-C-N bond angles [average = 175.5(6)°] are nearly linear with Mn-C bond distances of the two *trans* orientated cyano ligands of 2.013(6) Å. However, the Mn-C bond distance [1.939(6) Å] of the cyano ligand orientated *trans* towards the nitrogen atom of the 1,10-phenanthroline ligand in the equatorial plane is smaller than the same bond distances of the two *trans* orientated cyano ligands. The longer Mn-N(1P) bond distance of 2.032(5) Å compared to the Mn-C(2) distance of 1.939(6) Å is an indication of the larger *trans* influence of the cyano ligand on the ligands bonded *trans* towards it as discussed in § 5.3.2. The Mn-N(2P) bond distance is 2.268(5) Å, which compared to the Mn-N(1P) bond distance is an indication of the large *trans* influence of the nitrido ligand on ligands bonded *trans* to it.

The manganese(V) metal center is displaced by 0.268(5) Å out of the plane formed by the three carbon atoms of the cyano ligands and the nitrogen atom of the 1,10-phenanthroline ligand in the equatorial plane towards the nitrido ligand. This distortion and the small bite angle of the 1,10-phenanthroline ligand of 76.5(2)° led to considerable distortion of the coordination octahedron. The deviation of the N(10)-Mn-C [range from 97.2 (3)° to 99.9(2)°] and the C-Mn-N(2P) [range from 80.2(2)° to 88.8(2)°] angles from the required angle of 90° for the ideal octahedron is also an indication of this distortion of the coordination octahedron. The displacement of the manganese atom towards the nitrido ligand corresponds to those found for the [MnN(CN)₅]³⁻ [0.222(1) Å]²² and [MnN(py)(CN)₄]²⁻ anions [0.246(2) Å].²⁴

The bond distances and angles, as well as the geometries of the aromatic rings of the 1,10-phenanthroline ligand are (within experimental error) very similar as were found for [MoO(phen)(CN)₃]⁻.¹²

5.6. Structural correlations of the N,N'-substituted nitrido complexes of manganese(V).

A summary of the average bond lengths, ligand bite angles and $\nu_{(MX)}$ IR stretching frequencies for the N,N'-substituted nitridocyano complexes of the manganese(V) metal center described in this investigation, as well as literature examples of selected oxocyano and nitridocyano d^2 complexes of group 6 to 8 metal centers, are presented in Table 5.5.

Table 5.5: Bond data for selected isoelectronic N,N'-substituted cyano complexes of group 6 to 8 metal centers containing oxo or nitrido axial ligands.

Anion ^a	M=N or M=O (Å)	M-N ^b (Å)	D ^c (Å)	Bite angle (°)	M-N ^d (Å)	Mn-C ^e (Å)	N(10)-Mn-N(12) angle (°)	$\nu_{(MX)}$ ^f (cm ⁻¹)	Ref.
MnN(en)	1.532(4)	2.327(4)	0.290(2)	77.5(1)	2.074(4)	1.972(6)	176.5(2)	1022	⁹
MnN(bipy)	1.574(3)	2.244(3)	0.243(2)	75.2(1)	2.032(3)	1.959(4)	171.2(1)	1027	⁹
MnN(phen)	1.568(5)	2.268(5)	0.287(3)	76.5(1)	2.032(5)	1.939(6)	174.0(2)	1024	⁹
MoO(phen)	1.659(7)	2.363(7)	0.33(1)	71.0(2)	2.174(7)	2.092(9)	165.3(3)	970	¹²
WO(bipy)	1.735(7)	2.307(8)	not reported	70.8(3)	2.149(9)	2.149(13)	164.1(4)	973	¹³

^a Mn(en) = [MnN(en)(CN)₃]⁻; MnN(bipy) = [MnN(bipy)(CN)₃]⁻; MnN(phen) = [MnN(phen)(CN)₃]⁻; MoO(phen) = [MoO(phen)(CN)₃]²⁻; WO(bipy) = [WO(bipy)(CN)₃]²⁻;

^b *trans* to M=N or M=O bonds

^c Displacement of the central metal atom from the plane formed by the three carbon atoms of the cyano ligands and the nitrogen atom of the bidentate ligand.

^d M-N bond of the bidentate ligand *trans* to cyano ligand in equatorial plane.

^e M-C bond of the cyano ligand *trans* to the nitrogen atom of the bidentate ligand in the equatorial plane.

^f X = N³⁻ or O²⁻

⁹ This work

These N,N'-substituted nitrido complexes are the first bidentate substitution products of the nitridotetracyano complexes of manganese(V) that were isolated and studied crystallographically up to date. Addition of an excess of the bidentate ligand to a solution of the [MnN(CN)₄]²⁻ complex in water or water-ethanol mixtures afforded

crystals of the desired N,N'-substitution products of the $[\text{MnN}(\text{CN})_4]^{2-}$ complex. It is thought that when the $(\text{Ph}_4\text{P})_2[\text{MnN}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ complex dissolves in water, the $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ anion is formed due to hydrolysis in the presence of high concentrations of the aqua ligand. These complexes were crystallized with the large organic cations, $(\text{Ph}_4\text{P})^+$ and $(\text{Ph}_4\text{As})^+$, to give the desired products. The crystal structure determinations showed that the incoming bidentate ligand substituted the aqua ligand as well as one cyano ligand. The substitution of the aqua and the cyano ligands take place in a two-step process. The first step is the substitution of the aqua ligand *trans* to the nitrido ligand, followed by the ring-closing of the chelate with the simultaneous substitution of the cyano ligand in the equatorial plane. The sequence of these substitution steps were determined from the crystal structure determinations of $\text{Na}[\text{MoO}(\text{phen})(\text{CN})_3]\cdot 2\text{phen}^{12}$ and $(\text{Ph}_4\text{As})_2[\text{WO}(\text{pic})(\text{CN})_3]\cdot 2\text{H}_2\text{O}^{14}$ and the kinetic studies of the substitution reactions of $[\text{MoO}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ with 1,10-phenanthroline¹⁵ and $[\text{WO}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ with the picolinate anion¹⁷ respectively. Since these manganese(V) complexes are isoelectronic to the molybdenum(IV) and tungsten(IV) complexes, it can be expected that they will react according to the same mechanistic pathway. Since a $\text{M}-\text{OH}_2$ bond is usually much weaker than a $\text{M}-\text{CN}$ bond (this is especially the case in these complexes as a result of the large *trans* influence of the nitrido and oxo ligands) one would expect that the aqua ligand will be substituted first during the two-step process (see Table 2.2).

The large *trans* influence of the nitrido ligand is retained in the structures of the N,N'-substituted products of the $[\text{MnN}(\text{CN})_4]^{2-}/[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ anion. The Mn-N bond *trans* to the nitrido ligand is 0.25 Å longer in $[\text{MnN}(\text{en})(\text{CN})_3]^-$, 0.21 Å longer in $[\text{MnN}(\text{bipy})(\text{CN})_3]^-$ and 0.24 Å longer in $[\text{MnN}(\text{phen})(\text{CN})_3]^-$ compared to the Mn-N bond distance *trans* to the cyano ligand. The manganese(V) metal atom is also significantly displaced from the plane formed by the three carbon atoms and the nitrogen atom in the equatorial plane towards the nitrido ligand in these mentioned complexes. This is a frequently occurring phenomenon in octahedrally coordinated transition metal complexes containing one strong π -bonded ligand such as the nitrido or oxo ligands on the axis perpendicular to the plane containing the *cis*-bonded ligands.

The $[\text{MnN}(\text{en})(\text{CN})_3]^-$ anion has the shortest Mn=N bond distance [1.532(4) Å], while the $[\text{MnN}(\text{bipy})(\text{CN})_3]^-$ anion has the longest [1.574(3) Å] (Table 5.5). In comparison, the ethylenediamine ligand has the largest bite angle (77.5(1) °) and the 2,2'-bipyridine ligand has the smallest bite angle [75.2(1) °]. One would expect the increasing rigidity built into the carbon backbone of the bidentate ligand to result in smaller bite angles for ligands with a more rigid carbon backbone. Thus a smaller bite angle was expected for the 1,10-phenanthroline ligand than the 2,2'-bipyridine ligand. Some distortion is still allowed in the bond between the two aromatic rings of the 2,2'-bipyridine ligand, whereas the 1,10-phenanthroline ligand has a more rigid backbone with the extra carbon chain between carbon atoms C(4P) and C(7P) (see Figure 5.1, Figure 5.2 and Figure 5.3). Due to the single bonds between the atoms in the ethylenediamine ligand, it is expected to be the most flexible ligand of the series with the largest angles as well.

The IR stretching frequencies for the Mn=N bonds of the $[\text{MnN}(\text{en})(\text{CN})_3]^-$, $[\text{MnN}(\text{bipy})(\text{CN})_3]^-$ and $[\text{MnN}(\text{phen})(\text{CN})_3]^-$ are similar and it seems that no conclusion can be made from the small difference in these values as to the *trans* influence of the *trans* bonded nitrogen atoms on the nitrido ligands in these complexes. However, if the bond data are taken into account it seems that the *trans* influence of these nitrogen atoms decrease in the order of bipy > phen > en. The IR stretching frequencies also indicate that the nitrido ligand forms stronger bonds with the metal center compared to the oxo ligand (see Table 5.5).

The Mn=N and M=O (M = molybdenum and tungsten) stretching frequencies as well as the bond data for these two types of bonds in Table 5.5 indicate that the Mn=N bond is shorter, which is not surprising since the nitrido ligand is the one of the strongest π -bonding ligands known. The short Mn=N bond can also be attributed to the fact that the manganese(V) metal center has a smaller ionic radius compared to the Mo and W metal centers ($\text{Mn}^{\text{V}} = 0.33 \text{ \AA}$, $\text{Mo}^{\text{IV}} = 0.65 \text{ \AA}$ and $\text{W}^{\text{IV}} = 0.66 \text{ \AA}$).²⁶ This short bond distance can also be attributed to the charge on the manganese metal center (+5) compared to the molybdenum and tungsten (+4).

²⁶ Shannon, R.D., *Acta Cryst.*, **1976**, A32, 751.

The larger bite angles and shorter metal-to-ligand bond distances determined for the N,N'-bidentate ligands of the complexes of manganese(V) compared to the complexes of molybdenum(IV) and tungsten(IV) can also be explained in terms of the smaller ionic radius for the manganese(V) metal center than the molybdenum(IV) and tungsten(IV) metal centers (see Table 5.5).

The shorter Mn-C(2) bond distances compared to Mn-C bond distances of the two *trans*-bonded cyano ligands of the N,N'-bidentate substituted complexes can be explained in terms of the thermodynamic *trans* influence of the cyano ligand. The cyano ligand has a larger thermodynamic *trans* influence compared to the nitrogen atom of the N,N'-bidentate ligand and this would lead to a shortening of the Mn-C bond *trans* to the nitrogen atom in contrast to the two *trans* orientated cyano ligands with the slightly longer Mn-C bonds. The shorter Mn-C(2) bond distance can also be due the fact that the nitrogen atom of the N,N'-bidentate ligand has very weak or no π -bonding capability. This leads to extensive shortening of the Mn-C bond due to preferred backbonding from the metal to the π^* -orbital of the carbon atom of the cyano ligand.

The determination of the crystal structures of the $[\text{MnN}(\text{en})(\text{CN})_3]^-$, $[\text{MnN}(\text{bipy})(\text{CN})_3]^-$ and $[\text{MnN}(\text{phen})(\text{CN})_3]^-$ were of importance due to the fact that this series of ligands have never been investigated with the same *trans* bonded ligand as well as the same metal center. However, one cannot necessarily predict from these structure determinations whether the aqua ligand or the cyano ligand is substituted first and thus, it was also important to use a bidentate ligand with different donor atoms for similar bidentate substitution reactions. The results obtained from the crystallographic study of the substitution products of the reactions between the $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ complex and bidentate ligands with different donor atoms are described in Chapter 6.