4. Crystallographic Study of Different Monodentate Substituted Nitridotetracyano Complexes of Manganese(V).

4.1. Introduction

As mentioned in § 3.1, the $[TcN(H_2O)(CN)_4]^{2-}$,[1] $[ReN(H_2O)(CN)_4]^{2-}$,[2] $[ReN(CN)_5]^{3-}$,[3] $[ReN(N_3)(CN)_4]^{3-}$,[4] $[OsN(CN)_5]^{2-}$ [5] and $[OsN(OH)(CN)_4]^{2-}$ [6] complexes have already been synthesized in previous studies and the tetraphenylphosphonium or tetraphenylarsonium salts of these anions have been crystallographically characterized.

Recently, crystals of $(Ph_4P)_2[MnN(CN)_4]\cdot 2H_2O$,[7] $(Ph_4P)_2[MnN(py)(CN)_4]\cdot py\cdot H_2O$[7] and $[Rh(en)_3][MnN(CN)_5]\cdot H_2O$[8] suitable for X-ray crystallography were obtained and the crystal structures of these complexes were determined. Results from these structure determinations showed that the complexes have very short terminal nitrido-metal bonds (1.5 – 1.6 Å). This is an indication of the significant π-bond character of the metal-nitrogen bond; the nitrido ligand being the strongest π-donor known to date. The Mn=N bond in the five-coordinated $[MnN(CN)_4]^{2-}$ anion of 1.507(2) Å is the shortest nitrido-metal bond reported to date.[7]

The nitrido ligand displays a large *trans* influence on the ligands bonded *trans* to it. Thus, the *trans* Mn-C bond distance in the $[MnN(CN)_5]^{3-}$ anion[8] is *ca.* 0.25 Å longer

[1] Baldas, J.; Boas, J.F.; Colmanet, S.F.; Mackay, M.F., *Inorg. Chim. Acta*, **1990**, *170*, 233.
[2] Purcell W.; Potgieter I. M.; Damoense L. J.; Leipoldt J. G., *Transition Met. Chem*, 1992, **17**, 387.
[3] Purcell, W.; Potgieter, I.M.; Damoense, L.J.; Leipoldt, J.G., *Transition Met. Chem.*, **1991**, *16*, 473.
[4] Purcell, W.; Damoense, L.J.; Leipoldt, J.G., *Inorg. Chim. Acta*, **1992**, *195*, 217.
[5] Che, C.M.; Lam, M.H.; Mak, T.C.W., *J. Chem. Soc. Chem. Commun.*, **1989**, 1531.
[6] Van der Westhuizen, H.J.; Basson, S.S.; Purcell, W., *Transition Met. Chem.*, **1994**, *19*, 582.
[7] Bendix, J.; Meyer, K; Weyhermüller, T.; Bill, E.; Metzler-Nolte, N.; Wieghardt, K., *Inorg. Chem.*, **1998**, *37*, 1767.
[8] Bendix, J.; Deeth, R.J.; Weyhermüller, T.; Bill, E.; Wieghardt, K., *Inorg. Chem*, **2000**, *39*, 930.

than the *cis* Mn-C bond distances. If the bonding capability of the cyano ligand is taken into account, this case probably represents the lower limit on the *trans* influence in these types of complexes.

The crystal structure determination of the $(Ph_4P)_2[MnN(CN)_4] \cdot 2H_2O$ complex[7] has unequivocally established that the five-coordinate $[MnN(CN)_4]^{2-}$ anion does not contain an aqua ligand *trans* towards the nitrido ligand and that the water molecules of crystallization are not situated near this coordination site. The water molecules of crystallization form a hydrogen-bonding network with the terminal nitrogen atoms of the equatorial cyano ligands and are not located near the vacant sixth coordination site of the $[MnN(CN)_4]^{2-}$ anion. The sixth potential coordination site of the square-base pyramid of the anion is therefore vacant. In contrast, in the crystallographically characterized $(Ph_4As)_2[TcN(H_2O)(CN)_4] \cdot 5H_2O$ complex,[1] the anion is six coordinate with the Tc=N and Tc-OH$_2$ bond distances determined as 1.596(10) Å and 2.559(9) Å respectively. The isostructural $(Ph_4As)_2[ReN(H_2O)(CN)_4] \cdot 5H_2O$ complex[2] [Re=N = 1.639(8) Å, Re-OH$_2$ = 2.496(7) Å] also contains an aqua ligand bonded *trans* towards the nitrido ligand. Interestingly, the M-OH$_2$ bond distance of the above-mentioned aqua complexes increase on going from rhenium to technetium by 0.06(1) Å, whereas the M=N bond distance decrease by 0.043(9) Å. Thus, the Re=N bond is slightly less covalent than the corresponding Tc=N bond and much less covalent than the Mn=N bond, which exerts the strongest *trans* influence of the series, possibly rendering the water molecule uncoordinated.

A few monosubstituted nitridotetracyano complexes of manganese(V) were crystallized and crystallographically characterized during the course of this study. One of the main reasons was to determine the *trans* influence of the nitrido ligand on a series of ligands that have different electronic and steric parameters. Initial experiments showed that very high concentrations of these ligands were necessary to obtain the desired products and that these reactions were too fast to observe even on a third generation stopped-flow spectrophotometer (half-lives at [L] = 0.050 M shorter than 1 ms). Only crystals of the starting $(Ph_4P)_2[MnN(CN)_4] \cdot 2H_2O$ complex were obtained if low concentrations of the entering nucleophiles in aqueous media were used, thus, in certain cases trivalent cations had to be used to obtain crystals of the desired compounds from aqueous solutions of the entering nucleophiles.

4.2.   Experimental

The data collections for the X-ray structure determinations of these complexes were performed on a 1K Bruker SMART CCD system (University of the Witwatersrand), using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at ambient temperature (293 K), except for the crystal structure determination of [Rh(en)$_3$][MnN(NCS)(CN)$_4$]·H$_2$O, which was done at low temperature (173 K). The densities of the crystals were determined by flotation in benzene/diiodomethane.

All the structures were solved with conventional Patterson and Fourier methods, refined through full-matrix least-squares calculations using the SHELXL97[9] series of programmes, with $\Sigma(/Fo/-/Fc/)^2$ being minimised.   All non-hydrogen atoms were refined anisotropically, while the phenyl 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 Diamond[10] 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 monodentate substituted complexes investigated in this study is provided in Table 4.1.

---

[9] Sheldrick, G.M., SHELX-97, *Program for the refinement of crystal structures*, University of Göttingen, Germany, **1997**.
[10] Brandenburg, K.; Diamond (Ver. 2.1e), Crystal Impact GbR, Bonn, Germany, **2001**.

Table 4.1: **Crystallographic data for the different monodentate ligand substituted nitridotetracyano complexes of manganese(V).**

Crystal data	Mnncs [a]	Mncn4 [b]	Mn(3-pic) [c]	Mn(4-pic) [d]
Empirical formula	$C_{11}H_{26}N_{12}OSMnRh$	$C_{52}H_{44}N_5O_2P_2Mn$	$C_{64}H_{54}N_7P_2Mn$	$C_{61}H_{52.5}N_{6.5}OP_2Mn$
Formula weight	532.25	887.80	1038.02	1009.47
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.749(2)	12.103(2)	9.606(1)	10.292(2)
b (Å)	12.904(3)	12.337(2)	11.627(1)	13.106(2)
c (Å)	17.854(4)	16.781(2)	25.636(3)	20.557(3)
α (°)	90	97.511(3)	93.878(3)	79.521(3)
β (°)	90	108.993(3)	91.339(3)	87.217(4)
γ (°)	90	90.560(3)	105.962(3)	78.756(4)
Volume (Å^3)	2015.8(8)	2345.1(6)	2743.8(6)	2674.1(7)
Z	4	2	2	2
ρ_{exp} (g cm^{-3})	1.76	1.24	1.25	1.26
ρ_{calc} (g cm^{-3})	1.754	1.257	1.256	1.254
Crystal size (mm)	0.50 x 0.24 x 0.20	0.44 x 0.28 x 0.26	0.23 x 0.10 x 0.05	0.34 x 0.32 x 0.18
Absorption coefficient (mm^{-1})	1.578	0.395	0.346	0.354
F(000)	1080	924	1084	1054
θ range (°)	1.95 to 28.31	1.67 to 26.00	0.80 to 26.00	1.01 to 26.00
Index ranges	$-11 \le h \le 11$ $-17 \le k \le 14$ $-23 \le l \le 22$	$-14 \le h \le 14$ $-9 \le k \le 15$ $-20 \le l \le 20$	$-11 \le h \le 11$ $-14 \le k \le 10$ $-31 \le l \le 30$	$-9 \le h \le 12$ $-16 \le k \le 16$ $-25 \le l \le 24$
Reflections collected / unique / observed	12757 / 4904 / 4667	13960 / 9125 / 5979	16514 / 10692 / 4598	15957 / 10424 / 5042
R(int)	0.0214	0.0274	0.0682	0.0606
Completeness to 2 theta (° ; %)	28.31, 99.1	26.00, 99.0	26.00, 99.3	26.00, 99.0
T_{max}; T_{min}	0.729; 0.641	0.902; 0.876	0.983; 0.959	0.938; 0.877
Data / restraints / parameters	4904 / 0 / 250	9125 / 0 / 571	10692 / 0 / 668	10424 / 0 / 664
Goodness-of-fit on F^2	1.148	1.037	0.933	0.925
Final R indices [I > 2sigma(I)]	$R_1 = 0.0283$ $wR_2 = 0.0611$	$R_1 = 0.0456$ $wR_2 = 0.0963$	$R_1 = 0.0601$ $wR_2 = 0.1041$	$R_1 = 0.0524$ $wR_2 = 0.0990$
R indices (all data)	$R_1 = 0.0312$ $wR_2 = 0.0619$	$R_1 = 0.0849$ $wR_2 = 0.1094$	$R_1 = 0.1809$ $wR_2 = 0.1515$	$R_1 = 0.1429$ $wR_2 = 0.1275$
Largest diff. peak and hole (e.Å^{-3})	0.941 and -0.744	0.261 and -0.286	0.231 and -0.263	0.313 and -0.282

[a] Mnncs = $[Rh(en)_3][MnN(NCS)(CN)_4] \cdot H_2O$

[b] Mncn4 = $(Ph_4P)_2[MnN(CN)_4] \cdot 2H_2O$

[c] Mn(3-pic) = $(Ph_4P)_2[MnN(3\text{-pic})(CN)_4] \cdot (3\text{-pic})$

[d] Mn(4-pic) = $(Ph_4P)_2[MnN(4\text{-pic})(CN)_4]$

4.3. $[Rh(en)_3][MnN(NCS)(CN)_4] \cdot H_2O$

4.3.1.   Introduction

The preparation of the $[Rh(en)_3][MnN(NCS)(CN)_4] \cdot H_2O$ complex is reported in §
3.3.7.   A molecular diagram showing the numbering scheme of the anion is
presented in Figure 4.1 and selected bond distances and angles are given in Table
4.2 with a discussion highlighting some of the important aspects of the structure of
the $[MnN(NCS)(CN)_4]^{3-}$ anion presented thereafter. A comparison with other relevant
structures is given in § 4.7. Supplementary data containing complete lists of atomic
coordinates, anisotropic displacement parameters, bond distances and angles as
well as hydrogen coordinates are given in § A.1 in Appendix A.

The complex crystallized in the orthorhombic space group, $P2_12_12_1$, with four
molecules per unit cell. The chiral centre of the molecule is situated in the cation and
the conformation of the cation was determined as Λ??δ.[11] The rhodium metal center
of the trivalent cation is octahedrally coordinated to the six nitrogen atoms of three
1,2-diaminoethane ligands.   The average Rh-N bond distance of 2.087(3) Å
corresponds well with the same bond distances found in the $[Rh(en)_3]^{3+}$ cation of the
$[Rh(en)_3][MnN(CN)_5] \cdot H_2O$ complex[8] [Rh-N$_{(average)}$ = 2.079(5) Å].   The N-Rh-N bond
angles range from 82.9(1)° to 94.9(1)°, which are within the same limits found for the
$[Rh(en)_3]^{3+}$ cation [82.5(2)° to 94.7(2)°] of the $[Rh(en)_3][MnN(CN)_5] \cdot H_2O$ complex.
The nitrogen-carbon and carbon-carbon bond distances and angles correspond well
to those previously determined for $[Rh(en)_3][MnN(CN)_5] \cdot H_2O$.[8]

The $[Re(en)_3]^{3+}$ cation forms three weak intermolecular hydrogen-bonding contacts
[N(12)•••N(4) = 3.017(4) Å, N(31)•••N(3) = 3.309(4) Å, N(32)•••N(10) = 3.223(5) Å]
with two nitrogen atoms of the equatorial cyano ligands and the axial nitrido ligand.
Usually the nitrido ligand does not form any intermolecular contacts with the cations
or any of the solvents of crystallization present in the structure. The water molecule
of crystallization forms a weak hydrogen-bonding contact [O(1W)•••N(2) = 2.893(4) Å]
with one of the nitrogen atoms of one of the equatorial cyano ligands. The hydrogen-

---

[11] Purcell, K.F.; Kotz, J.C., *Inorganic Chemistry*, W. B. Sanders Company, **1977**, 642.

bonding between a water molecule of crystallization and one of the nitrogen atoms of an equatorially bonded cyano ligand seems to be a frequently occurring phenomenon for this type of transition metal complex.
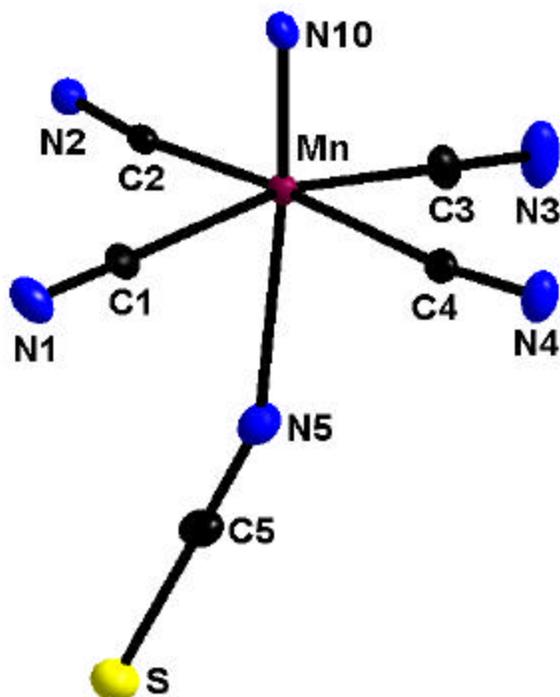

Figure 4.1: **Molecular diagram showing the numbering scheme and displacement ellipsoids (30 % probability) of the [MnN(NCS)(CN)$_4$]$^{3-}$ anion. The cations and solvent molecules are omitted for clarity.**

Table 4.2: **Selected bond distances (Å) and angles (°) for the [MnN(NCS)(CN)$_4$]$^{3-}$ anion.**

Bond distances (Å)			
Mn-N(10)	1.540(3)	Mn-C(3)	1.995(4)
Mn-C(1)	2.004(3)	Mn-C(2)	2.007(3)
Mn-C(4)	2.017(3)	Mn-N(5)	2.298(3)
C(1)-N(1)	1.157(4)	C(2)-N(2)	1.152(4)
C(3)-N(3)	1.155(5)	C(4)-N(4)	1.160(4)
N(5)-C(5)	1.154(5)	C(5)-S	1.664(4)
Bond angles (°)			
N(10)-Mn-C(3)	99.26(15)	N(10)-Mn-C(1)	94.44(15)
C(3)-Mn-C(1)	166.25(15)	N(10)-Mn-C(2)	93.68(14)
C(3)-Mn-C(2)	85.84(13)	C(1)-Mn-C(2)	94.40(12)
N(10)-Mn-C(4)	95.36(15)	C(3)-Mn-C(4)	86.69(13)
C(1)-Mn-C(4)	90.99(13)	C(2)-Mn-C(4)	169.08(13)
N(10)-Mn-N(5)	174.60(13)	C(3)-Mn-N(5)	84.87(14)
C(1)-Mn-N(5)	81.52(13)	C(2)-Mn-N(5)	83.11(12)
C(4)-Mn-N(5)	88.31(13)	N(1)-C(1)-Mn	177.5(3)
N(2)-C(2)-Mn	173.3(3)	N(3)-C(3)-Mn	178.4(3)
N(4)-C(4)-Mn	173.0(3)	C(5)-N(5)-Mn	158.3(3)
N(5)-C(5)-S	177.6(3)		

4.3.2. Results and discussion

The manganese(V) metal center is octahedrally coordinated to the nitrido ligand, four cyano ligands and the thiocyanate ligand *trans* to the nitrido ligand. The Mn=N bond distance of 1.540(3) Å is longer than the corresponding bond distance of 1.499(8) Å in the [MnN(CN)$_5$]$^{3-}$ complex.[8] The average Mn-C bond distance between the central metal atom and the carbon atoms of the cyano ligands of 2.006(3) Å and the average C=N bond distance of 1.156(4) Å are comparable to the same bond distances found in [MnN(CN)$_4$]$^{2-}$ of 1.983(2) and 1.160(2) Å respectively. The average Mn-C-N bond angle is 175.5(3)° and is nearly linear as expected for this type of moiety. The Mn-N bond distance of 2.298(3) Å between the manganese(V) metal center and the

thiocyanate ligand is slightly longer than the Mn-C bond distance of 2.243(7) Å between the manganese(V) metal center and the cyano ligand coordinated *trans* to the nitrido in the $[MnN(CN)_5]^{3-}$ anion.[8] The manganese(V) metal center can be considered as a hard acid due to the high formal charge on the metal atom and will preferably bind to the hard base part of the thiocyanate ion, i.e. the nitrogen atom. The N(5)-C(5) bond distance is 1.154(5) Å and the C(5)-S bond distance is 1.664(4) Å. The Mn-N(5)-C(5) angle is 158.3(3)° and the N(5)-C(5)-S angle is 177.6(3)°. The same results were observed for the $[ReO(NCS)(CN)_4]^{2-}$ complex[12] [N-C$_{(NCS)}$ = 1.15(2) Å, C-S$_{(NCS)}$ = 1.62(2) Å, Re-N-C = 169(1)°, N-C-S = 176(1)°].

The manganese(V) metal center of the $[MnN(NCS)(CN)_4]^{3-}$ anion is displaced by 0.196(2) Å from the best plane formed by the four carbon atoms of the cyano ligands. This large distortion of the coordination polyhedron is also reflected in the deviations from the expected rectangular values for the N(10)-Mn-C and C-Mn-N(5) bond angles which range from 99.26(15)° to 93.68(14)° and 88.31(13)° to 81.52(13)° respectively. The displacement of the manganese atom towards the nitrido ligand along the N(10)=Mn-N(5) axis forces the *cis*-bonded cyano ligands and the N(5) atom of the thiocyanate ligand closer together as indicated by smaller than 90° C-Mn-N(5) bond angles. The same displacement was found to be 0.222(1) Å for the $[MnN(CN)_5]^{3-}$ anion.[8] These results seem to be ambiguous, since it is well known that the cyano ligand has a larger *trans* influence than the thiocyanate ligand, whereas the above-mentioned results seem to indicate that the thiocyanate ligand has a larger *trans* influence.

---

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

4.4. $(Ph_4P)_2[MnN(CN)_4]\cdot 2H_2O$[7]

4.4.1. Introduction

The preparation of the $(Ph_4P)_2[MnN(CN)_4]\cdot 2H_2O$ complex is reported in § 3.3.5. A molecular diagram showing the numbering scheme of the anion is presented in Figure 4.2 and selected bond distances and angles are given in Table 4.3 with a discussion highlighting some of the important aspects of the $[MnN(CN)_4]^{2-}$ anion presented thereafter. A comparison with other relevant structures is given in § 4.7. Supplementary data containing complete lists of atomic coordinates, anisotropic displacement parameters, bond distances and angles as well as hydrogen coordinates are given in § A.2 in Appendix A.

Although this crystal structure was already described in the literature,[7] the crystals obtained for the structure determination were isolated from a 2-methylpyridine solution and we thought initially that crystals of the $(Ph_4P)_2[MnN(2\text{-pic})(CN)_4]$ complex were isolated. However, the crystal structure determination showed that crystals of the $(Ph_4P)_2[MnN(CN)_4]\cdot 2H_2O$ complex were isolated instead. Reasons for the isolation of the $(Ph_4P)_2[MnN(CN)_4]\cdot 2H_2O$ complex instead of the $(Ph_4P)_2[MnN(2\text{-pic})(CN)_4]$ complex may be that the latter complex has a very low stability constant (K_1) or the $(Ph_4P)_2[MnN(CN)_4]$ complex may have a lower crystallization energy compared to the $(Ph_4P)_2[MnN(2\text{-pic})(CN)_4]$ complex.

The $(Ph_4P)_2[MnN(CN)_4]\cdot 2H_2O$ compound crystallizes in a triclinic space group, $P\bar{1}$, with two molecules per unit cell. The structure of $(Ph_4P)_2[MnN(CN)_4]\cdot 2H_2O$ consists of well separated $(Ph_4P)^+$ cations and $[MnN(CN)_4]^{2-}$ anions as well as two water molecules of crystallization. The bond distances and angles within the two $(Ph_4P)^+$ cations were normal and in good agreement with those found in previous reported structure determinations.[3,7,13] The $(Ph_4P)^+$ cations are tetrahedral with average P-C bond distances of 1.794(2) Å. The C-P-C bond angles ranged from 106.4(1) ° to 111.6(1) ° and the geometries, bond distances and angles of the phenyl rings were within normal limits.

---

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

Interestingly, the two water molecules of crystallization are not located near the vicinity of the vacant sixth coordination site of the $[MnN(CN)_4]^{2-}$ anion, but instead they form weak intermolecular hydrogen bonding contacts with two nitrogen atoms [O1W•••N2 = 2.984(3) Å, O2W•••N4 = 3.054(4) Å] of two of the cyano ligands (see Figure 4.2).   Thus, the anions and the water molecules form an infinite chain structure in the solid state.   It is also very interesting that the nitrido ligand is not involved in any hydrogen bonding. The same results were observed for the reported structure.[7]
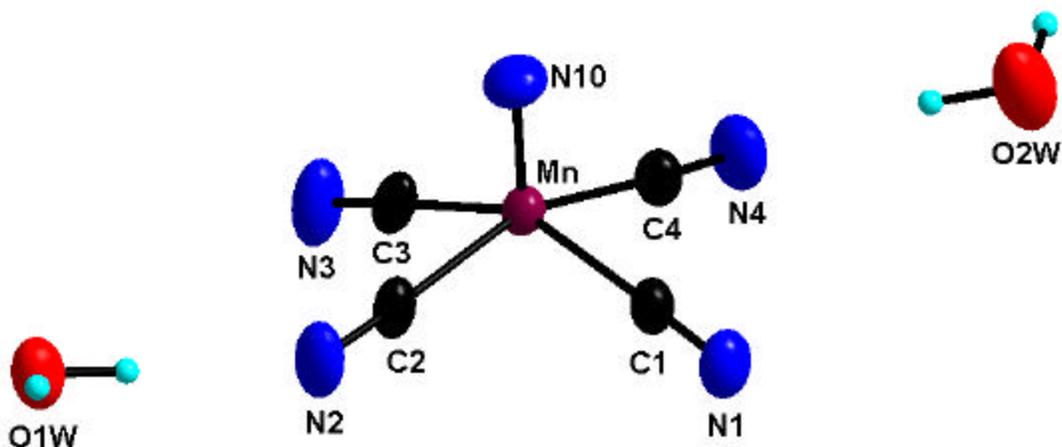
Figure 4.2:   **Molecular diagram showing the numbering scheme and displacement ellipsoids (30 % probability) of the [MnN(CN)$_4$]$^{2-}$ anion. The cations are omitted for clarity.**

Table 4.3: Selected bond distances (Å) and angles (°) for the [MnN(CN)$_4$]$^{2-}$ anion.

Bond distances (Å)					
	a	b		a	b
Mn-N(10)	1.497(2)	1.507(2)	C(1)-N(1)	1.141(3)	1.162(2)
Mn-C(1)	1.959(3)	1.985(2)	C(2)-N(2)	1.143(3)	1.160(2)
Mn-C(3)	1.964(3)	1.995(2)	C(3)-N(3)	1.139(3)	1.159(2)
Mn-C(2)	1.974(3)	1.976(2)	C(4)-N(4)	1.145(3)	1.160(2)
Mn-C(4)	1.982(3)	1.974(2)			
Bond angles (°)					
	a	b		a	b
N(10)-Mn-C(1)	105.47(12)	100.4(1)	N(4)-C(4)-Mn	176.0(3)	177.2(2)
N(10)-Mn-C(3)	104.11(12)	99.7(1)	C(1)-Mn-C(3)	150.38(11)	159.9(1)
N(10)-Mn-C(2)	101.16(12)	105.1(1)	C(1)-Mn-C(2)	86.06(10)	86.9(1)
N(10)-Mn-C(4)	100.36(13)	105.7(1)	C(3)-Mn-C(2)	86.70(10)	89.6(1)
N(1)-C(1)-Mn	178.4(2)	177.3(2)	C(1)-Mn-C(4)	87.37(10)	85.4(1)
N(2)-C(2)-Mn	177.3(3)	176.1(2)	C(3)-Mn-C(4)	88.95(10)	87.5(1)
N(3)-C(3)-Mn	177.2(3)	176.3(2)	C(2)-Mn-C(4)	158.46(11)	149.0(1)

[a] experimental data   [b] literature reported data[7]

4.4.2. Results and discussion

The manganese(V) metal center of the anion is coordinated to a nitrido ligand and four cyano ligands. The five coordinate [MnN(CN)$_4$]$^{2-}$ anion showed a square-based pyramidal coordination geometry with the nitrido ligand in the apical position. The Mn≡N bond distance of 1.497(2) Å is extremely short and is indicative of extensive pπ-dπ ligand-to-metal interaction. The average Mn-C bond distance is 1.970(3) Å and the average C≡N bond distance is 1.142(3) Å with an average Mn-C-N bond angle of 177.2(3)°. These bond distances are within experimental error nearly the same as those found [Mn≡N = 1.507(2) Å and C≡N$_{(average)}$ = 1.983(2) Å] for the reported structure.[7] The slight difference in these bond distances may be due to the fact that these structure determinations were performed at different temperatures, room temperature for this determination *versus* -173(2) °C for the reported structure.

The manganese(V) metal center is displaced by 0.435(1) Å from the plane formed by the four carbon atoms of the four cyano ligands in the equatorial plane towards the nitrido ligand. This distortion of the coordination polyhedron is also indicated by the deviation of the N(10)-Mn-C bond angles [N(10)-Mn-C bond angles ranged from 100.36(13)° to 105.47(12)°] from the expected 90° for the ideal square-based pyramid. This mode of distortion, coupled with the large *trans* influence of the nitrido ligand, may lead to such a large repulsion between the equatorially bonded cyano ligands and the ligand in the *trans* position that weak coordinators, like the aqua ligand, coordinates very weakly or do not coordinate in the vacant coordination site *trans* to the nitrido ligand.

This is one of only two structure determinations of nitridotetracyano complexes where the sixth coordination site *trans* towards the nitrido ligand is vacant. However, there are some discrepancies in the reported crystal structure of the other five-coordinate nitridotetracyano complex of rhenium(V), *e.g.* $K_2[ReN(CN)_4] \cdot H_2O$.[14] One interesting fact about this structure determination is that the nitrido ligand of a neighbouring anion is situated close to the vacant sixth coordination site and thus, a stacking of the anions one on top of the other is observed. The results from this study showed that the cyano ligands are nitrogen bonded and that the Re-N-C moiety is bent. The average N≡C bond distance in this structure is 1.31 Å and the rhenium atom is displaced out of the plane formed by the four nitrogen atoms away from the nitrido ligand. Thus, the results from the $[ReN(CN)_4]^{2-}$ structure determination are totally opposite to the results obtained from numerous crystal structure determinations performed on the nitridotetracyano complexes of technetium(V)[1], rhenium(V)[2,3,4] and osmium(VI)[6] in this laboratory. Usually, the central metal ion is displaced towards the nitrido ligand and the cyano ligands are carbon bonded except where HCN acts as the entering ligand, then the HCN ligand is nitrogen bonded.[15] However, it is possible that the $[ReN(CN)_4]^{2-}$ structure determination is not entirely correct since the structure was determined from only a small number of film-intensity data and some disorder may be present in the crystal structure.

---

[14] Davies, W.O.; Johnson, N.P.; Johnson, P., *Chem. Commun.*, **1969**, 736.
[15] Smit, J.P.; Purcell, W.; Roodt, A.; Leipoldt, J.G., *J. Chem. Soc., Chem. Commun.*, **1993**, 1388.

4.5. (Ph$_4$P)$_2$[MnN(3-pic)(CN)$_4$]·(3-pic)

4.5.1. Introduction

The preparation of the (Ph$_4$P)$_2$[MnN(3-pic)(CN)$_4$]·(3-pic) complex is reported in §
3.3.9. A molecular diagram showing the numbering scheme of the anion is
presented in Figure 4.3 and selected bond distances and angles are given in Table
4.4 with a discussion highlighting some of the important aspects of the [MnN(3-
pic)(CN)$_4$]$^{2-}$ anion presented thereafter. A comparison with other relevant structures
is given in § 4.7. Supplementary data containing complete lists of atomic
coordinates, anisotropic displacement parameters, bond distances and angles as
well as hydrogen coordinates are given in § A.3 in Appendix A.

The complex crystallized in a triclinic space group, $P\bar{1}$, with two molecules per unit
cell. The structure of (Ph$_4$P)$_2$[MnN(3-pic)(CN)$_4$]·(3-pic) consists of well separated
(Ph$_4$P)$^+$ cations, [MnN(3-pic)(CN)$_4$]$^{2-}$ anions and 3-methylpyridine molecules. The
bond distances and angles within the two (Ph$_4$P)$^+$ cations are normal and in good
agreement with those found in the previous reported structure determinations
containing this cation.[3,7,13] The (Ph$_4$P)$^+$ cations are tetrahedral with average P-C
bond distances of 1.789(4) Å. The C-P-C bond angles range from 107.4(2) ° to
113.0(2) ° and the bond distances, angles and geometries of the phenyl rings are
within normal limits for these moieties.

The 3-methylpyridine molecule of crystallization in the unit cell is not situated near
the anion molecule and thus, no interactions between these two moieties can take
place. Interestingly, no water molecules of crystallization were detected during the
solution of this structure determination. The water molecule present in the crystals of
(Ph$_4$P)$_2$[MnN(py)(CN)$_4$]·py·H$_2$O formed weak hydrogen-bonding contacts to one of
the nitrogen atoms of a cyano group of the anions and the nitrogen atom of the
pyridine molecule of crystallization. This trend was however not observed in the
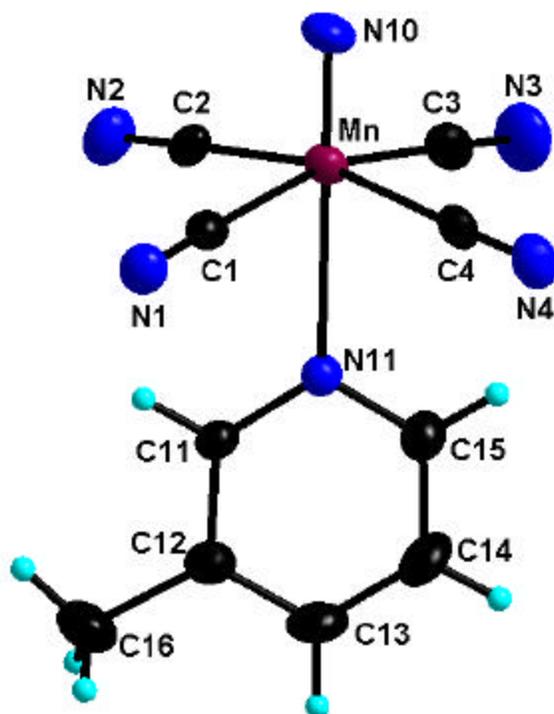crystal structure of (Ph$_4$P)$_2$[MnN(3-pic)(CN)$_4$]·(3-pic).

Figure 4.3: Molecular diagram showing the numbering scheme and displacement ellipsoids (30 % probability) of the [MnN(3-pic)(CN)$_4$]$^{2-}$ anion. The cations and solvent molecule are omitted for clarity.

Table 4.4: Selected bond distances (Å) and angles (°) for the [MnN(3-pic)(CN)$_4$]$^{2-}$ anion.

Bond distances (Å)			
Mn-N(10)	1.523(4)	Mn-C(4)	1.989(5)
Mn-C(3)	1.992(5)	Mn-C(2)	1.995(5)
Mn-C(1)	1.996(5)	Mn-N(11)	2.431(4)
C(1)-N(1)	1.150(5)	C(2)-N(2)	1.148(5)
C(3)-N(3)	1.151(5)	C(4)-N(4)	1.151(5)
N(11)-C(15)	1.318(5)	N(11)-C(11)	1.348(5)
C(11)-C(12)	1.376(6)	C(12)-C(13)	1.362(6)
C(12)-C(16)	1.514(7)	C(13)-C(14)	1.367(7)
C(14)-C(15)	1.380(7)		

Bond angles (°)			
N(10)-Mn-C(4)	96.9(2)	N(10)-Mn-C(3)	97.5(2)
C(4)-Mn-C(3)	88.94(18)	N(10)-Mn-C(2)	97.4(2)
C(4)-Mn-C(2)	165.66(19)	C(3)-Mn-C(2)	90.54(19)
N(10)-Mn-C(1)	97.84(19)	C(4)-Mn-C(1)	86.97(18)
C(3)-Mn-C(1)	164.50(19)	C(2)-Mn-C(1)	89.75(18)
N(10)-Mn-N(11)	179.44(18)	C(4)-Mn-N(11)	82.82(16)
C(3)-Mn-N(11)	83.00(17)	C(2)-Mn-N(11)	82.89(16)
C(1)-Mn-N(11)	81.66(15)	N(1)-C(1)-Mn	176.2(4)
N(2)-C(2)-Mn	177.4(4)	N(3)-C(3)-Mn	178.0(5)
N(4)-C(4)-Mn	178.6(5)	C(15)-N(11)-C(11)	115.8(4)
C(15)-N(11)-Mn	121.7(3)	C(11)-N(11)-Mn	122.3(3)
N(11)-C(11)-C(12)	124.8(4)	C(13)-C(12)-C(11)	117.4(5)
C(13)-C(12)-C(16)	122.2(5)	C(11)-C(12)-C(16)	120.4(5)
C(12)-C(13)-C(14)	119.3(5)	C(13)-C(14)-C(15)	119.2(5)
N(11)-C(15)-C(14)	123.4(5)		

4.5.2.   Results and discussion

The manganese(V) metal center of the $[MnN(3\text{-pic})(CN)_4]^{2-}$ anion is octahedrally coordinated to a nitrido ligand, four cyano ligands and the 3-methylpyridine ligand. The nitrogen atom of the 3-methylpyridine ligand is bonded *trans* to the nitrido ligand. The Mn=N bond distance of 1.523(4) Å is comparatively short.[7] The average Mn-C bond distance between the metal center and the carbon atoms of the cyano ligands is 1.993(5) Å and the average C=N bond distance is 1.150(5) Å with an average Mn-C-N bond angle of 177.6(5)°. The same bond distances were observed for the cyano groups in $[MnN(py)(CN)_4]^{2-}$ [Mn-C $_{(average)}$ = 1.997(5) Å and C=N $_{(average)}$ = 1.157(5) Å].[7] The Mn-N(11) bond distance is 2.431(4) Å and this bond distance is 0.041 Å shorter than the same bond distance in $[MnN(py)(CN)_4]^{2-}$ anion [2.472(4) Å]. This is an indication of the higher electron density on the aromatic ring of the 3-methylpyridine ligand compared to the unsubstituted pyridine ligand. The bond distances and angles of the both the bonded and free 3-methylpyridine molecules are in good agreement with those found in literature.[16]

The manganese-bonded atoms in the $[MnN(3\text{-pic})(CN)_4]^{2-}$ anion have a distorted octahedral geometry. The manganese(V) metal center is displaced by 0.257(2) Å towards the nitrido ligand above the plane formed by the four carbon atoms of the cyano ligands. This displacement is comparable to the same displacement found in the $[MnN(py)(CN)_4]^{2-}$ anion of 0.246(2) Å.[7] The distortion of the coordination octahedron is also evident from the deviation of the N(10)-Mn-C and C-Mn-N(11) bond angles from the angular 90° expected for the ideal octahedron, which ranged from 97.84(19)° to 96.9(2)° and 83.00(17)° to 81.66(15)° respectively. The smaller than 90° angle for the C-Mn-N(11) bond angles, as well as the displacement of the metal center towards the nitrido ligand, forces the *cis*-bonded cyano ligands and the nitrogen atom (N(11)) of the 3-methylpyridine ligand together. This distortion coupled with the large *trans* influence of the nitrido ligand is responsible for the longer than expected Mn-N(11) bond distance of 2.431(4) Å.

---

[16] Mautner, F.A.; Goher, M.A.S., *Crys. Res. Technol.*, **1990**, *25*, 1271.

4.6. (Ph$_4$P)$_2$[MnN(4-pic)(CN)$_4$]·0.5(4-pic)·H$_2$O

4.6.1. Introduction

The preparation of the (Ph$_4$P)$_2$[MnN(4-pic)(CN)$_4$]·0.5(4-pic)·H$_2$O complex is reported in § 3.3.10. A molecular diagram showing the numbering scheme of the anion is presented in Figure 4.4 and selected bond distances and angles are given in Table 4.5 with a discussion highlighting some of the important aspects of the [MnN(4-pic)(CN)$_4$]$^{2-}$ anion presented thereafter. A comparison with other relevant structures is given in § 4.7. Supplementary data containing complete lists of atomic coordinates, anisotropic displacement parameters, bond distances and angles as well as hydrogen coordinates are given in § A.4 in Appendix A.

The compound crystallized in a triclinic space group, $P\bar{1}$, with two molecules per unit cell. The 4-methylpyridine molecule was disordered around the centre of symmetry in the unit cell. The disorder was successfully modelled by a split atom model. The nitrogen atom and the carbon of the methyl group shared the same coordinates in the unit cell and were refined with half occupancy for each atom.

The structure of (Ph$_4$P)$_2$[MnN(4-pic)(CN)$_4$]·0.5(4-pic)·H$_2$O consists of well separated (Ph$_4$P)$^{+}$ cations, [MnN(4-pic)(CN)$_4$]$^{2-}$ anions, 4-methylpyridine and water molecules. The (Ph$_4$P)$^{+}$ cations have a tetrahedral geometry with an average P-C bond distance of 1.794(4) Å. The C-P-C bond angles ranged from 107.4(2) ° to 112.0(2) ° and the bond distances, angles and geometry of the phenyl rings were within normal limits for these moieties.[3,7,13]

The water molecule of crystallization formed weak intermolecular hydrogen-bonding contacts [O(1W)•••N(2) = 2.959(5) Å] to one of the cyano ligands of the [MnN(4-pic)(CN)$_4$]$^{2-}$ anion. No interaction between the water molecule and the 4-methyl pyridine molecule was detected. It is interesting that the nitrido ligand does not take part in any interactions with the molecules of crystallization, suggesting that the nitrido ligand has a low basicity compared to the nitrogen atoms of the *cis*-bonded cyano ligands.
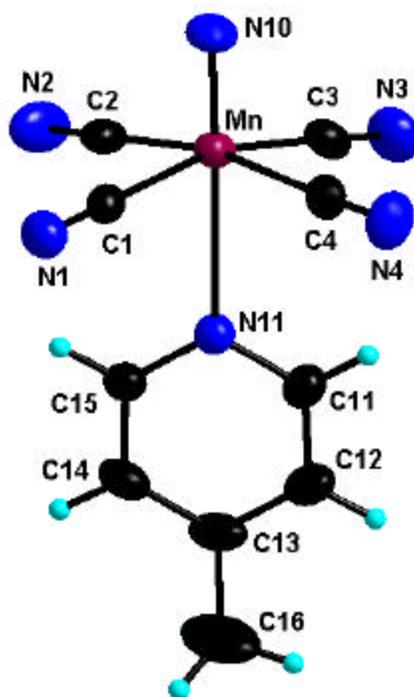
Figure 4.4: Molecular diagram showing the numbering scheme and displacement ellipsoids (30 % probability) of the [MnN(4-pic)(CN)$_4$]$^{2-}$ anion. The cations and solvent molecules are omitted for clarity.

Table 4.5: Selected bond distances (Å) and angles (°) for the [MnN(4-pic)(CN)$_4$]$^{2-}$ anion.

Bond distances (Å)			
Mn-N(10)	1.514(3)	Mn-C(4)	1.980(4)
Mn-C(1)	1.990(4)	Mn-C(3)	1.994(4)
Mn-C(2)	1.997(4)	Mn-N(11)	2.429(3)
C(1)-N(1)	1.149(4)	C(2)-N(2)	1.141(4)
C(3)-N(3)	1.144(4)	C(4)-N(4)	1.153(4)
N(11)-C(11)	1.318(4)	N(11)-C(15)	1.334(4)
C(11)-C(12)	1.381(5)	C(13)-C(16)	1.521(5)
C(12)-C(13)	1.368(5)	C(14)-C(15)	1.379(5)
C(13)-C(14)	1.364(5)		

Bond angles (°)			
N(10)-Mn-C(4)	97.42(16)	N(10)-Mn-C(1)	97.99(16)
C(4)-Mn-C(1)	87.62(14)	N(10)-Mn-C(3)	98.24(16)
C(4)-Mn-C(3)	88.75(15)	C(1)-Mn-C(3)	163.69(14)
N(10)-Mn-C(2)	95.56(15)	C(4)-Mn-C(2)	167.02(15)
C(1)-Mn-C(2)	90.79(15)	C(3)-Mn-C(2)	89.19(15)
N(10)-Mn-N(11)	177.53(14)	C(4)-Mn-N(11)	85.02(13)
C(1)-Mn-N(11)	82.50(12)	C(3)-Mn-N(11)	81.35(12)
C(2)-Mn-N(11)	82.00(12)	N(1)-C(1)-Mn	178.6(3)
N(2)-C(2)-Mn	178.9(3)	N(3)-C(3)-Mn	178.5(4)
N(4)-C(4)-Mn	177.3(4)	C(11)-N(11)-C(15)	116.1(3)
C(11)-N(11)-Mn	121.5(2)	C(15)-N(11)-Mn	121.6(2)
N(11)-C(11)-C(12)	123.8(4)	C(13)-C(12)-C(11)	119.8(4)
C(14)-C(13)-C(12)	116.9(4)	C(14)-C(13)-C(16)	121.7(5)
C(12)-C(13)-C(16)	121.3(5)	C(13)-C(14)-C(15)	120.0(4)
N(11)-C(15)-C(14)	123.4(4)		

4.6.2. Results and discussion

The manganese(V) atom in the $[MnN(4\text{-pic})(CN)_4]^{2-}$ is octahedrally coordinated to the nitrido ligand, four cyano ligands and the 4-methylpyridine ligand. The nitrogen atom of the 4-methylpyridine molecule is bonded *trans* to the nitrido with cyano ligands bonded *cis* in the equatorial plane. The Mn=N bond distance of 1.514(3) Å is comparatively short to that of the same bond [1.525(4) Å] in $[MnN(py)(CN)_4]^{2-}$. The average Mn-C bond distance between the manganese(V) metal center and the cyano ligands is 1.990(4) Å and the average C=N bond distance is 1.147(4) Å and a near linear average Mn-C-N bond angle of 178.3(4)°. The Mn-N(11) bond distance is 2.429(3) Å and is only slightly shorter than the same bond distance of 2.472(4) Å in $[MnN(py)(CN)_4]^{2-}$. This shortening of the Mn-N(11) bond distance can be attributed to the higher electron density on the aromatic ring of the 4-methylpyridine ligand compared to the unsubstituted pyridine ligand.[7] The bond distances and angles as well as the geometry of the 4-methylpyridine ligand are in good agreement with those found in literature.[17]

The $[MnN(4\text{-pic})(CN)_4]^{2-}$ anion has a distorted octahedral geometry with the manganese(V) metal atom displaced by 0.253(2) Å from the best plane formed by the four carbon atoms of the cyano ligands towards the nitrido ligand. This type of distortion is also reflected in the deviation from rectangular values for the N(10)-Mn-C and C-Mn-N(11) angles which range from 98.24(16)° to 95.56(15) and 85.02(13)° to 81.35(12)° respectively. This displacement is indicative of the large *trans* influence of the nitrido ligand towards the *trans* bonded ligands with the longer than expected Mn-N(11) bond distance of 2.429(3) Å and it is comparable to the same displacement of 0.246(2) Å in the $[MnN(py)(CN)_4]^{2-}$ anion.[7]

---

[17] Harris, J.D.; Eckles, W.E.; Hepp, A.F.; Duraj, S.A.; Fanwick, *Inorg. Chim. Acta*, **2002**, *338*, 99.

4.7. Structural correlations of the monodentate substituted nitridotetracyano complexes of manganese(V).

A summary of the average bond lengths and $\nu_{(M\equiv N)}$ IR stretching frequencies for the monosubstituted nitridotetracyano complexes of the manganese(V) metal center described in this investigation, as well as literature examples of selected oxotetracyano and nitridotetracyano d^2 complexes of group 6 to 8 metal centers is presented in Table 4.6.

Table 4.6: Bond data for selected isoelectronic tetracyano complexes of group 6 to 8 metal centers containing oxo or nitrido axial ligands.

Anion	M≡N (Å)	M-C [a] (Å)	M-L [b] (Å)	D [c] (Å)	$\nu_{(M\equiv N)}$ (cm^{-1})	Ref.
[MnN(NCS)(CN)$_4$]$^{3-}$	1.540(3)	2.006(3)	2.298(3)	0.196(2)	1056	[d]
[MnN(CN)$_4$]$^{2-}$	1.497(2)	1.970(3)	-	0.435(1)	1105	[d]
[MnN(CN)$_4$]$^{2-}$	1.507(2)	1.983(2)	-	0.436	1094	[7]
[MnN(3-pic)(CN)$_4$]$^{2-}$	1.523(4)	1.993(5)	2.431(3)	0.257(2)	1040	[d]
[MnN(4-pic)(CN)$_4$]$^{2-}$	1.514(3)	1.990(4)	2.429(3)	0.253(3)	1043	[d]
[MnN(py)(CN)$_4$]$^{2-}$	1.525(4)	1.997(4)	2.472(4)	0.246(2)	1041	[7]
[MnN(CN)$_5$]$^{3-}$	1.499(8)	1.990(6)	2.243(7)	0.222(1)	1011	[8]
[TcN(H$_2$O)(CN)$_4$]$^{2-}$	1.596(10)	2.11(2)	2.559(9)	0.35	1100	[1]
[ReN(CN)$_5$]$^{3-}$	1.68(1)	2.12(1)	2.39(1)	0.31	1040	[3]
[ReN(H$_2$O)(CN)$_4$]$^{2-}$	1.64(1)	2.11(1)	2.496(7)	0.35	1060	[2]
[ReN(N$_3$)(CN)$_4$]$^{3-}$	1.65(2)	2.11(1)	2.36(2)	0.34	1074	[4]
[OsN(OH)(CN)$_4$]$^{2-}$	1.606(5)	2.068(9)	2.123(5)	0.26	1050	[6]
[OsN(CN)$_5$]$^{2-}$	1.647(7)	2.082(8)	2.353(8)	not reported	1050	[5]

[a] Equatorial M-CN bonds   [b] *trans* to M≡N bonds

[c] Displacement of the central metal atom from the plane formed by the four cyano ligands

[d] This work

It is interesting to note that when the bulky organic cations, Ph$_4$P$^+$ or Ph$_4$As$^+$, were used in aqueous medium, only crystals of the (Ph$_4$P)$_2$[MnN(CN)$_4$]·2H$_2$O complex for example were obtained and not of the CN$^-$, NCS$^-$ and N$_3^-$ substituted complexes (see § 3.3.7 and 3.3.8).[8] Thus, even in a solution containing a large excess of cyanide the (Ph$_4$P)$_2$[MnN(CN)$_4$]·2H$_2$O complex was isolated and not the expected (Ph$_4$P)$_3$[MnN(CN)$_5$] complex. However, these nitridotetracyano complexes, for

example $(Ph_4P)_2[MnN(CN)_4]\cdot 2H_2O$, were very convenient starting materials for the preparation of other substitution products, like $(Ph_4P)_2[MnN(3\text{-pic})(CN)_4]\cdot(3\text{-pic})$. It was necessary to crystallize the picoline (3- and 4-methylpyridine) complexes from neat solutions of the $(Ph_4P)_2[MnN(CN)_4]$ complex in the relevant picoline solution. The picoline ligands of both the $(Ph_4P)_2[MnN(3\text{-pic})(CN)_4]\cdot(3\text{-pic})$ and $(Ph_4P)_2[MnN(4\text{-pic})(CN)_4]\cdot 0.5(4\text{-pic})\cdot H_2O$ complexes were lost over time from the crystals of these complexes. The robust $[Rh(en)_3]^+$ tervalent cation was used to crystallize the $[MnN(NCS)(CN)_4]^{3-}$ trianion from a very concentrated thiocyanate solution (1 M). The crystals of the $[Rh(en)_3][MnN(NCS)(CN)_4]\cdot H_2O$ complex lost the water molecules of crystallization as well and therefore these crystals were used directly after isolation to circumvent this problem.

The M≡N bonds in the nitridotetracyano complexes of the manganese(V) metal center are extremely short, much shorter compared to the other nitridotetracyano complexes of the second and third row metals of group 6, 7 and 8 (1.6 -1.8 Å). The M≡N bond strength or bond distances of the nitrido complexes of group 7 (manganese, technetium, rhenium) cannot be compared directly if only the ionic radii of these metal centers are taken into account, because there is a large difference between the ionic radii of these metals (Mn^V = 0.33 Å, Tc^V = 0.60 Å and Re^V = 0.58 Å).[18] Thus, the ionic radii decrease in the order technetium(V) = rhenium(V) > manganese(V). This may explain the decrease in the metal-*cis* cyano bond distance from technetium(V) and rhenium(V) to manganese(V). However, the covalent radii for all the members of group 7 metals are taken to be 1.35 Å from the Cambridge Structural Data Base and the difference between covalent radii of the metal atoms of group 6, 7 and 8 are negligibly small.

These short M≡N bonds are indicative of strong $p\pi\text{-}d\pi$ ligand-to-metal interaction and a large *trans* influence of the nitrido ligand. This is not surprising in view of the fact that the nitrido ligand is one of the strongest π-electron donors known.

The determination of the crystal structures of the nitridotetracyano complexes of manganese(V) showed that the metal ion is located in the center of the equatorial

---

[18] Shannon, R.D., *Acta Cryst.*, **1976**, *A32*, 751.

plane formed by the carbon atoms of the four *cis* cyano ligands with the nitrido ligand in one of the axial positions above this plane. The manganese(V) ion is displaced from the equatorial plane towards the nitrido ligand. The amount of displacement of the heavy atom from the square plane formed by the four carbon atoms of the cyano ligands, as well as the Mn=N bond distance, is sensitive to the nature of the entering ligand and may be used as an indication of the bond strength and *trans* influence of the entering ligand (see Table 4.6).

The large *trans* influence of the nitrido ligand is evident in the monodentate substituted complexes since the metal-ligand bonds *trans* to the nitrido ligand in these complexes are longer than expected (Table 4.6). The metal atom is displaced from the plane formed by the four carbon atoms of the cyano ligands. The distortion of the angles of the coordination octahedron are also proof of this fact (see § 4.3.2, 4.4.2, 4.5.2 and 4.6.2). 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.

It is very interesting to note that the $[MnN(H_2O)(CN)_4]^{2-}$ anion could not be isolated with the addition of the typical large organic cations, Ph_4P^+ and Ph_4As^+, whereas both the $[TcN(H_2O)(CN)_4]^{2-}$ [1] and $[ReN(H_2O)(CN)_4]^{2-}$ [2] anions were crystallized from solution using these cations. It seems that the nitrido ligand in the manganese(V) complexes has such a large *trans* influence that the aqua ligand is only associated with the *trans* coordination site in solution (high concentration of the aqua ligand) and that upon the crystallization of the $[MnN(H_2O)(CN)_4]^{2-}$ complex with these large organic cations the *trans* coordination site is vacant.

As mentioned earlier, the results from the crystal structure determination of the $[MnN(NCS)(CN)_4]^{3-}$ complex showed that the Mn=N bond distance is 0.04 Å longer than the same bond distance in the $[MnN(CN)_5]^{3-}$ complex. The $[MnN(NCS)(CN)_4]^{3-}$ complex [0.196(2) Å] also has a smaller distortion from the ideal octahedral geometry compared to the $[MnN(CN)_5]^{3-}$ complex [8] [0.222(1) Å]. These results seem to indicate that the thiocyanato ligand has a larger *trans* influence compared to the cyano ligand, which is the opposite from what is expected with the cyano ligand having the larger

trans influence.   The manganese(V) metal center is considered to be a hard acid since it is bonded to the hard base part of the NCS^- ligands, the nitrogen atom, in the $[MnN(NCS)(CN)_4]^{3-}$ anion.

The Mn=N bond distances, the Mn-N(11) bond distances *trans* to the nitrido and the displacements of the manganese(V) metal center in $[MnN(py)(CN)_4]^{2-}$,[7] $[MnN(3-pic)(CN)_4]^{2-}$ and $[MnN(4-pic)(CN)_4]^{2-}$ are comparable.   Thus, the methyl groups of the 3-methylpyridine and 4-methylpyridine ligands have only a very small effect on the electron density of the aromatic ring and these ligands have similar bonding capability compared to the unsubstituted pyridine ligand.

The stretching frequency of the Mn=N bond [ν(Mn=N)] is a more sensitive parameter to compare the relative *trans* influences of the entering ligands.   The ν(Mn=N) values indicate that the *trans* influences (and probably the bond strengths) decrease in order of N^{3-} >> CN^- > NCS^- > 4-pic ~ py ~ 3-pic > H_2O (see § 3.3.8 and Table 4.6).

The structure determinations of the monodentate substituted products are of importance since it was found that the $[MnN(CN)_4]^{2-}$ complex has an unoccupied coordination site *trans* to the nitrido ligand.   The $[MnN(CN)_5]^{3-}$ complex can be considered to be at the opposite side of the spectrum due to the fact that the cyano ligand is a strong coordinating ligand.   It was therefore important to determine if weaker coordinating ligands will also coordinate to the $[MnN(CN)_4]^{2-}$ complex. However, it is important to remember that the $[MnN(H_2O)(CN)_4]^{2-}$ complex may exist in solution and that the aqua ligand is substituted by monodentate ligands.

The structural determinations not only provided more information on the anionic metal complexes, but also the type and number of cations.   The number of water molecules of crystallization as well as the interactions of these water molecules with the anions and cations were also determined.   This knowledge provides valuable information with regard to determining the reaction mechanism, *e.g.*, firstly very high concentrations of the free ligand (a 1M thiocyanate solution for example) are necessary to crystallize the anionic complexes.   Secondly, the additional free ligand crystallizing with some of the anions may have a retarding effect on the reaction rate

in a dissociative mechanism and free ligand contribution must be included in determining the total free ligand concentrations. These structure determinations were a prerequisite for the accurate characterization of the complexes employed as reactants and some insight into the substitution reactions of these complexes also has been gained.