
6. Crystal Structure Determinations of the N,O-Substituted Complexes of Manganese(V) and Molybdenum(IV).

6.1. Introduction

A thorough crystallographic study of the complexes and ligands used, as well as a kinetic study of the products formed is of crucial importance in order to obtain correlations between the parameters observed in the solid state (X-ray crystallography) and in solution (kinetics). A thorough understanding of the bonding modes of ligands as determined by X-ray crystallography therefore is important in the rationalization of the tendencies observed during a kinetic study. As some of the ligands used in this study were only investigated to a limited extent, it was imperative to try and obtain crystal structures and kinetic data on the whole series of ligands, as well as for different metal centers and different *trans* axial ligands (like oxo and nitrido ligands).

It is known that the dioxotetracyano complexes of group 6 to 8 metals can, upon protonation, undergo bidentate substitution by replacement of an aqua or hydroxo ligand *trans* to oxo ligand as well as replacement of one of the equatorial cyano ligands. A limited number of crystallographic^{1,2,3} and kinetic studies^{4,5,6} were performed with pyridine-carboxylate (picolinate) ligands as bidentate ligands. Previous studies performed on the molybdenum(IV) and tungsten(IV) systems showed that one of the oxygen atoms of the carboxylic group first reacts with the oxotetracyano complex and is bonded *trans* to the oxo ligand. The nitrogen atom of

¹ Basson, S.S.; Leipoldt, J.G.; Potgieter, I.M., *Inorg. Chim. Acta*, **1984**, *87*, 71.

² Szklarzewicz, J.; Samotus, A.; Alcock, N.W.; Moll, M., *J. Chem. Soc. Dalton Trans.*, **1990**, 2959.

³ Leipoldt, J.G.; Basson, S.S.; Roodt, A.; Potgieter, I.M., *Transition Met. Chem.*, **1986**, *11*, 323.

⁴ Leipoldt, J.G.; Basson, S.S.; Potgieter, I.M.; Roodt, A., *Inorg. Chem.*, **1987**, *26*, 57.

⁵ Samotus, A.; Kanas, A.; Glug, W.; Szklarzewicz, J., *Transition Met. Chem.*, **1991**, *16*, 614.

⁶ Roodt, A.; Basson, S.S.; Leipoldt, J.G., *Polyhedron*, **1994**, *13*, 599.

the pyridine moiety then substitutes one of the cyano ligands in the equatorial plane in a ring-closure step. No crystallographic data exists up to date for the substitution products of the reaction between the pyridine carboxylate ligands and nitridotetracyano complexes of the group 6 to 8 metal centers. In this chapter the reaction products of some of the pyridine carboxylate ligands and the nitridotetracyano complex of manganese(V) and the oxotetracyano complex of molybdenum(IV), which were characterized by means of X-ray crystallography, will be discussed.

6.2. Experimental

The data collections for the X-ray structure determinations of the N,O-substituted nitrido and oxo complexes were performed on a 1K Bruker SMART CCD system (University of the Witwatersrand), using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at ambient temperature (293 K), except for the $(\text{Ph}_4\text{As})_2[\text{MnN}(\text{quin})(\text{CN})_3]$ complex, 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 SHELXL97⁷ series of programmes, with $\Sigma(|F_o| - |F_c|)^2$ being minimized. 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 \AA , methyl C-H = 0.96 \AA , amine N-H = 0.89 \AA and aromatic C-H = 0.96 \AA). The hydrogen atoms of the water molecules of crystallization were determined geometrically from difference Fourier maps. The program Diamond⁸ 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 picolinate and related complexes of molybdenum(IV) and manganese(V) is provided

⁷ Sheldrick, G.M., SHELX-97, *Program for the refinement of crystal structures*, University of Göttingen, Germany, 1997.

⁸ Brandenburg, K.; Diamond (Ver. 2.1e), Crystal Impact GbR, Bonn, Germany, 2001.

6. STRUCTURES OF N,O-SUBSTITUTED COMPLEXES

in Table 6.1.

Table 6.1: Crystallographic data for the different picolinate and related complexes of manganese(V) and molybdenum(IV).

Crystal data	Mnpic ^a	Mnquin ^b	Mopic ^c
Empirical formula	C ₅₇ H ₅₂ N ₅ O ₆ As ₂ Mn	C ₆₁ H ₅₂ N ₅ O ₅ As ₂ Mn	C ₅₇ H ₅₀ N ₄ O ₆ As ₂ Mo
Formula weight	1107.82	1139.86	1132.79
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$\bar{P}1$	$\bar{P}1$	$\bar{P}1$
a (Å)	13.535(2)	13.401(3)	13.523(2)
b (Å)	13.790(2)	13.408(3)	13.540(2)
c (Å)	17.080(2)	17.140(3)	17.155(2)
α (°)	87.798(3)	72.09(3)	88.029(3)
β (°)	69.375(3)	88.53(3)	69.480(3)
γ (°)	61.450(3)	64.62(3)	62.962(2)
Volume (Å ³)	2587.9(7)	2627.2(9)	2590.7(5)
Z	2	2	2
ρ _{exp} (g cm ⁻³)	1.40	1.41	1.44
ρ _{calc} (g cm ⁻³)	1.452	1.441	1.452
Crystal size (mm)	0.35 x 0.20 x 0.20	0.36 x 0.28 x 0.16	0.32 x 0.16 x 0.14
Absorption coefficient (mm ⁻¹)	1.580	1.557	1.575
F(000)	1136	1168	1152
θ range (°)	1.29 to 28.50	1.26 to 26.00	1.28 to 26.00
Index ranges	-18 ≤ h ≤ 15 -18 ≤ k ≤ 18 -22 ≤ l ≤ 22	-15 ≤ h ≤ 16 -16 ≤ k ≤ 16 -20 ≤ l ≤ 21	-13 ≤ h ≤ 16 -15 ≤ k ≤ 16 -11 ≤ l ≤ 21
Reflections collected / unique / observed	24640 / 13060 / 5555	20888 / 10221 / 7434	15068 / 10114 / 6703
R(int)	0.0628	0.0991	0.0293
Completeness to 2 theta (° ; %)	28.50, 99.6	26.00, 98.9	26.00, 99.2
T _{max} ; T _{min}	0.729; 0.691	0.779; 0.599	0.802; 0.746
Data / restraints / parameters	13060 / 0 / 640	10221 / 0 / 667	10114 / 0 / 631
Goodness-of-fit on F ²	0.838	1.033	1.005
Final R indices [I > 2σ(I)]	R ₁ = 0.0495 wR ₂ = 0.0973	R ₁ = 0.0642 wR ₂ = 0.1708	R ₁ = 0.0453 wR ₂ = 0.1012
R indices (all data)	R ₁ = 0.1502 wR ₂ = 0.1190	R ₁ = 0.0919 wR ₂ = 0.1868	R ₁ = 0.0852 wR ₂ = 0.1178
Largest diff. peak and hole (e.Å ⁻³)	1.202 and -0.866	1.782 and -1.084	0.755 and -0.615

^a Mnpic = (Ph₄As)₂[MnN(pic)(CN)₃]·4H₂O

^b Mnquin = (Ph₄As)₂[MnN(quin)(CN)₃]·3H₂O

^c Mopic = (Ph₄As)₂[MoO(pic)(CN)₃]·3H₂O

6.3. $(\text{Ph}_4\text{As})_2[\text{MnN}(\text{pic})(\text{CN})_3]\cdot 4\text{H}_2\text{O}$

6.3.1. Introduction

The preparation of the $(\text{Ph}_4\text{As})_2[\text{MnN}(\text{pic})(\text{CN})_3]\cdot 4\text{H}_2\text{O}$ complex and growth of the crystals used for collection of the intensity data were reported in § 3.3.14. A molecular diagram showing the numbering scheme of the anion is presented in Figure 6.1 and selected bond distances and angles are given in Table 6.2 with a discussion highlighting some of the important aspects of the $[\text{MnN}(\text{pic})(\text{CN})_3]^{2-}$ anion presented thereafter. A comparison with other relevant structures is given in § 6.6. Supplementary data containing complete lists of atomic coordinates, anisotropic displacement parameters, bond distances and angles as well as hydrogen coordinates are given in § A.8 in Appendix A.

The dark red crystals lost solvent molecules over time and cracked, making them unsuitable for X-ray analysis. They were therefore used immediately after filtration from the solution. The complex crystallized in the triclinic space group, $P\bar{1}$, with two molecules per unit cell.

The crystal structure of $(\text{Ph}_4\text{As})_2[\text{MnN}(\text{pic})(\text{CN})_3]\cdot 4\text{H}_2\text{O}$ consisted of discrete $(\text{Ph}_4\text{As})^+$ cations and $[\text{MnN}(\text{pic})(\text{CN})_3]^{2-}$ anions. The bond distances and angles within the $(\text{Ph}_4\text{As})^+$ cations were normal and in good agreement with those found in other crystal structures containing the $(\text{Ph}_4\text{As})^+$ cation.^{9,10} The $(\text{Ph}_4\text{As})^+$ cations are tetrahedral with average As-C bond distances of 1.905(4) Å. The C-As-C bond angles range from 107.0(2)° to 112.5(2)° and the geometries of the phenyl rings were within the normal limits.

A few short intermolecular contacts between the water of crystallization molecules and the $[\text{MnN}(\text{pic})(\text{CN})_3]^{2-}$ anion were detected: $[\text{O}(1\text{W})\cdots\text{O}(3\text{W}) = 2.74\text{Å}$, $\text{O}(1\text{W})\cdots\text{N}(1) = 2.84\text{ Å}$, $\text{O}(2\text{W})\cdots\text{O}(3\text{W}) = 2.58\text{ Å}$, $\text{O}(2\text{W})\cdots\text{O}(11) = 2.74\text{ Å}$, $\text{O}(4\text{W})\cdots\text{O}(12) = 2.78\text{ Å}]$. However, these short contacts cannot be attributed to

⁹ Van der Westhuizen, H.J.; Basson, S.S.; Purcell, W., *Transition Met. Chem.*, **1994**, 19, 582.

¹⁰ Purcell W., Potgieter I. M., Damoense L. J. en Leipoldt J. G., *Transition Met. Chem.*, **1992**, 17, 387.

hydrogen bonding alone, because the hydrogen atoms of the water molecules of crystallization could not be determined accurately from the difference Fourier-map.

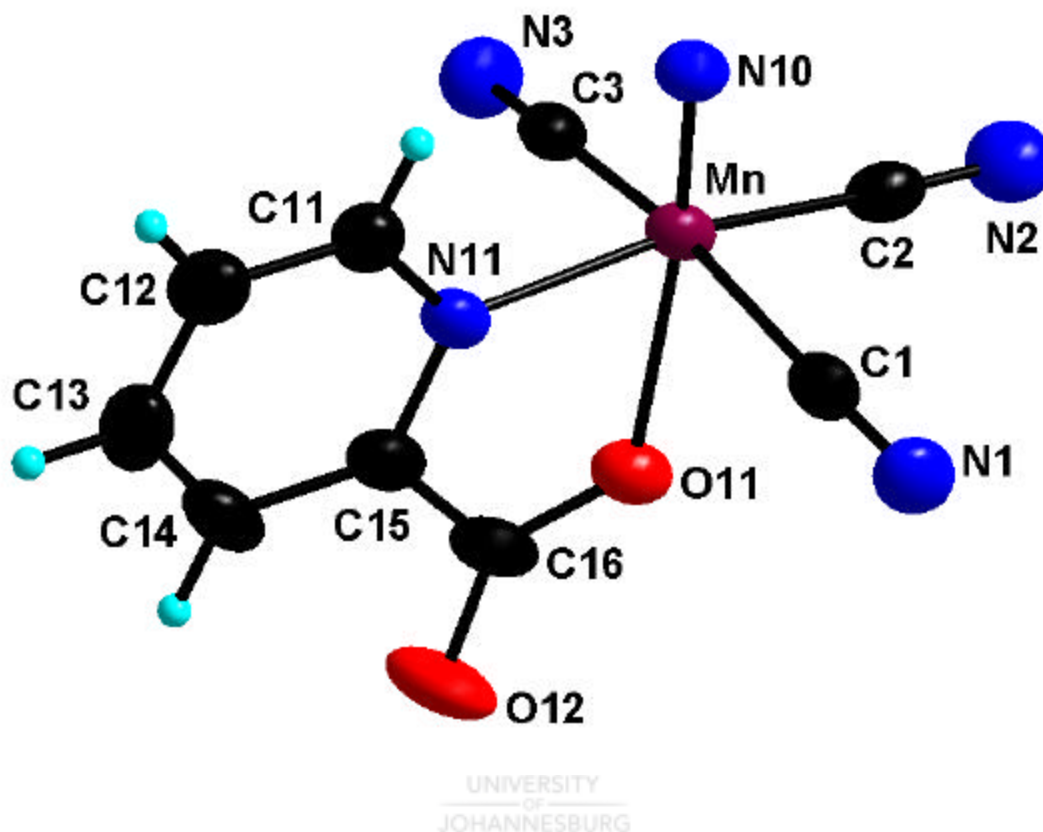


Figure 6.1: Molecular diagram showing the numbering scheme and displacement ellipsoids (30 % probability) of the $[\text{MnN}(\text{pic})(\text{CN})_3]^{2-}$ anion. The cations and solvent molecules are omitted for clarity.

Table 6.2: Selected bond distances (Å) and angles (°) for the $[\text{MnN}(\text{pic})(\text{CN})_3]^{2-}$ anion.

Bond distances (Å)			
Mn-N(10)	1.538(3)	Mn-C(2)	1.931(5)
Mn-C(1)	1.998(5)	Mn-C(3)	1.999(5)
Mn-N(11)	2.045(3)	Mn-O(11)	2.214(3)
C(1)-N(1)	1.154(5)	C(2)-N(2)	1.150(5)
C(3)-N(3)	1.142(5)	N(11)-C(11)	1.345(5)
N(11)-C(15)	1.354(5)	C(11)-C(12)	1.362(6)
C(12)-C(13)	1.365(7)	C(13)-C(14)	1.371(7)
C(14)-C(15)	1.397(6)	C(15)-C(16)	1.502(6)
C(16)-O(12)	1.242(5)	C(16)-O(11)	1.261(5)
Bond angles (°)			
N(10)-Mn-C(2)	97.27(18)	N(10)-Mn-C(1)	97.91(18)
C(2)-Mn-C(1)	85.99(17)	N(10)-Mn-C(3)	98.84(17)
C(2)-Mn-C(3)	86.74(18)	C(1)-Mn-C(3)	162.45(18)
N(10)-Mn-N(11)	95.85(17)	C(2)-Mn-N(11)	166.76(17)
C(1)-Mn-N(11)	93.96(15)	C(3)-Mn-N(11)	89.51(15)
N(10)-Mn-O(11)	171.93(16)	C(2)-Mn-O(11)	90.78(16)
C(1)-Mn-O(11)	82.15(15)	C(3)-Mn-O(11)	81.99(14)
N(11)-Mn-O(11)	76.12(13)	N(1)-C(1)-Mn	175.9(4)
N(2)-C(2)-Mn	176.0(4)	N(3)-C(3)-Mn	178.0(4)
C(11)-N(11)-C(15)	118.1(4)	C(11)-N(11)-Mn	124.2(3)
C(15)-N(11)-Mn	117.5(3)	N(11)-C(11)-C(12)	123.2(5)
C(11)-C(12)-C(13)	118.8(5)	C(12)-C(13)-C(14)	120.0(5)
C(13)-C(14)-C(15)	118.9(5)	N(11)-C(15)-C(14)	120.9(5)
N(11)-C(15)-C(16)	115.2(4)	C(14)-C(15)-C(16)	123.9(5)
O(12)-C(16)-O(11)	126.3(5)	O(12)-C(16)-C(15)	117.9(5)
O(11)-C(16)-C(15)	115.7(4)	C(16)-O(11)-Mn	115.1(3)

6.3.2. Results and discussion

The manganese(V) atom is octahedrally coordinated to a nitrido ligand, three cyano ligands and the nitrogen atom of the aromatic ring as well as one of the oxygen atoms of the carboxylate group of the picolate ligand in the $[\text{MnN}(\text{pic})(\text{CN})_3]^{2-}$ anion. The nitrogen atom of the picolate ligand is bonded *trans* to one of the equatorial cyano ligands and the oxygen atom is bonded *trans* to the nitrido ligand. The very short Mn=N bond distance of 1.538(3) Å suggests strong π - $d\pi$ ligand-to-metal interaction. The Mn-C bonds of the two *trans* orientated cyano ligands [average = 1.999(5) Å] have similar bond distances, while the Mn-C(2) bond distance [1.931(5) Å] of the cyano ligand that is orientated *trans* towards the nitrogen atom of the picolate ligand is shorter than similar bond distances of the *trans* orientated cyano ligands. The Mn-C-N moieties are nearly linear with an average bond angle of 176.6(4)°. The Mn-N(11) bond distance is 2.045(3) Å and the Mn-O(11) bond distance is 2.214(3) Å. The longer than expected Mn-O(11) bond distance is an indication of the large *trans* influence of the nitrido ligand towards the *trans*-bonded ligand, in this case the oxygen atom of the carboxylic group of the picolate ligand.

The coordination polyhedron of the $[\text{MnN}(\text{pic})(\text{CN})_3]^{2-}$ anion has a distorted octahedral geometry. The central manganese atom is displaced by 0.259(2) Å from the plane formed by the three carbon atoms of the cyano ligands and the nitrogen atom of the picolate ligand. This displacement and the small bite angle of 76.1(1)° of the bidentate ligand causes considerable distortion of the coordination octahedron. This distortion is also evident in the average N(10)-Mn-C [range from 97.27(18)° to 98.84(17)°] bond angles as well as the average C-Mn-O(11) [range from 81.99(14)° to 90.78(16)°] bond angles, which deviates considerably from the required 90° for the ideal octahedron. The displacement of the manganese(V) metal atom towards the nitrido ligand corresponds with the similar displacement (0.331 Å) found for the $[\text{WO}(\text{pic})(\text{CN})_3]^{2-}$ anion.³

The bond distances and angles of the picolate ligand in $[\text{MnN}(\text{pic})(\text{CN})_3]^{2-}$ are in good agreement with those found in $[\text{WO}(\text{pic})(\text{CN})_3]^{2-}$.³

6.4. $(\text{Ph}_4\text{As})_2[\text{MnN}(\text{quin})(\text{CN})_3]\cdot 3\text{H}_2\text{O}$

6.4.1. Introduction

The preparation of the $(\text{Ph}_4\text{As})_2[\text{MnN}(\text{quin})(\text{CN})_3]\cdot 3\text{H}_2\text{O}$ complex and growth of the crystals used for collection of the intensity data were reported in § 3.3.15. A molecular diagram showing the numbering scheme of the anion is presented in Figure 6.2 and selected bond distances and angles are given in Table 6.3 with a discussion highlighting some of the important aspects of the $[\text{MnN}(\text{quin})(\text{CN})_3]^{2-}$ anion presented thereafter. A comparison with other relevant structures is given in § 6.6. Supplementary data containing complete lists of atomic coordinates, anisotropic displacement parameters, bond distances and angles as well as hydrogen coordinates are given in § A.9 in Appendix A.

The red crystals lost solvent molecules over time and cracked, thus making them unsuitable for X-ray analysis. They were therefore used immediately after filtration from the solution. The data collection was done at low temperature (-100(2) °C) to prevent the loss of the water molecules.

The complex crystallized in the triclinic space group, $P\bar{1}$, with two molecules per unit cell. The crystal structure of $(\text{Ph}_4\text{As})_2[\text{MnN}(\text{quin})(\text{CN})_3]\cdot 3\text{H}_2\text{O}$ consists of discrete $(\text{Ph}_4\text{As})^+$ cations, $[\text{MnN}(\text{quin})(\text{CN})_3]^{2-}$ anions and water molecules of crystallization. The bond distances and angles within the $(\text{Ph}_4\text{As})^+$ cations are normal and in good agreement with those found in other structures containing the $(\text{Ph}_4\text{As})^+$ cation.^{3,9,10} The $(\text{Ph}_4\text{As})^+$ cations are tetrahedral with average As-C bond distances of 1.912(5) Å. The C-As-C bond angles range from 106.1(2)° to 111.2(2)° and the bond distances and angles of the carbon atoms of the phenyl rings are within normal limits.

One of the water molecules of crystallization has a very short intermolecular contact [$\text{O}(1\text{W})\cdots\text{O}(12) = 2.52 \text{ \AA}$] with the non-coordinated oxygen atom [O(12)] of the carboxylate group of the quinaldinate ligand. Short intermolecular contacts were also observed between one of the other water molecules and the oxygen [O(12)], between two water molecules and between one water molecule and the nitrogen

atom of one of the cyano ligands [$O(2W)\cdots O(12) = 2.87 \text{ \AA}$, $O(2W)\cdots O(3W) = 2.88 \text{ \AA}$, $O(3W)\cdots N(3) = 2.89 \text{ \AA}$]. The hydrogen atoms of the water molecules could be detected, but unfortunately they could not be refined satisfactorily from the Fourier-difference map.

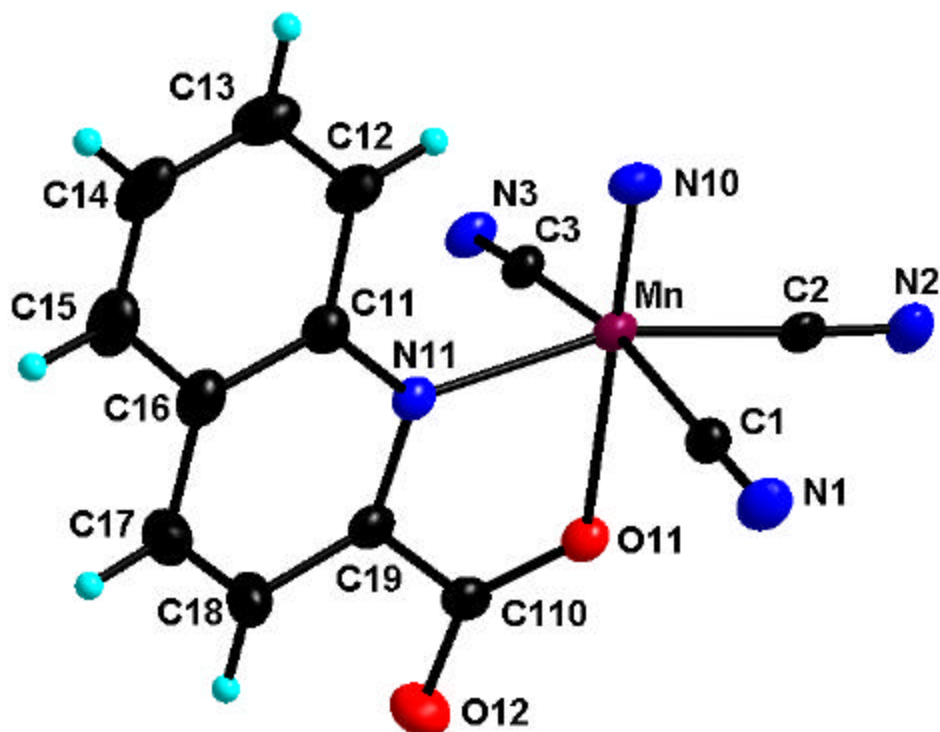


Figure 6.2: Molecular diagram showing the numbering scheme and displacement ellipsoids (30 % probability) of the $[MnN(quin)(CN)_3]^{2-}$ anion. The cations and solvent molecules are omitted for clarity.

Table 6.3: Selected bond lengths (Å) and angles (°) for the $[\text{MnN}(\text{quin})(\text{CN})_3]^{2-}$ anion.

Bond distances (Å)			
Mn-N(10)	1.523(5)	Mn-C(2)	1.984(5)
Mn-C(3)	1.999(5)	Mn-C(1)	2.003(5)
Mn-N(11)	2.110(4)	Mn-O(11)	2.168(4)
C(1)-N(1)	1.157(7)	C(2)-N(2)	1.136(7)
C(3)-N(3)	1.161(6)	N(11)-C(19)	1.331(7)
N(11)-C(11)	1.404(6)	C(11)-C(12)	1.397(8)
C(11)-C(16)	1.423(8)	C(12)-C(13)	1.394(8)
C(13)-C(14)	1.388(9)	C(14)-C(15)	1.337(9)
C(15)-C(16)	1.441(8)	C(16)-C(17)	1.408(9)
C(17)-C(18)	1.356(8)	C(18)-C(19)	1.404(8)
C(19)-C(110)	1.511(7)	C(110)-O(12)	1.254(6)
C(110)-O(11)	1.256(6)		
Bond angles (°)			
N(10)-Mn-C(2)	94.9(2)	N(10)-Mn-C(3)	97.3(2)
C(2)-Mn-C(3)	88.8(2)	N(10)-Mn-C(1)	96.2(2)
C(2)-Mn-C(1)	87.8(2)	C(3)-Mn-C(1)	166.3(2)
N(10)-Mn-N(11)	103.9(2)	C(2)-Mn-N(11)	161.2(2)
C(3)-Mn-N(11)	90.17(18)	C(1)-Mn-N(11)	88.78(18)
N(10)-Mn-O(11)	178.88(19)	C(2)-Mn-O(11)	84.87(18)
C(3)-Mn-O(11)	81.58(18)	C(1)-Mn-O(11)	84.88(18)
N(11)-Mn-O(11)	76.37(15)	N(1)-C(1)-Mn	178.7(4)
N(2)-C(2)-Mn	177.8(5)	N(3)-C(3)-Mn	177.4(5)
C(19)-N(11)-C(11)	116.7(4)	C(19)-N(11)-Mn	115.1(3)
C(11)-N(11)-Mn	128.0(3)	C(12)-C(11)-N(11)	121.0(5)
C(12)-C(11)-C(16)	118.5(5)	N(11)-C(11)-C(16)	120.5(5)
C(13)-C(12)-C(11)	121.0(6)	C(14)-C(13)-C(12)	119.9(6)
C(15)-C(14)-C(13)	121.4(6)	C(14)-C(15)-C(16)	120.7(6)
C(17)-C(16)-C(11)	119.4(5)	C(17)-C(16)-C(15)	122.1(6)
C(11)-C(16)-C(15)	118.5(6)	C(18)-C(17)-C(16)	119.2(5)
C(17)-C(18)-C(19)	119.0(6)	N(11)-C(19)-C(18)	125.0(5)
N(11)-C(19)-C(110)	116.0(4)	C(18)-C(19)-C(110)	119.0(5)
O(12)-C(110)-O(11)	126.5(5)	O(12)-C(110)-C(19)	118.0(5)
O(11)-C(110)-C(19)	115.5(4)	C(110)-O(11)-Mn	116.2(3)

6.4.2. Results and discussion

The manganese(V) atom is octahedrally coordinated to a nitrido ligand, three cyano ligands and the nitrogen atom of the aromatic pyridine ring, as well as to one of the oxygen atoms of the carboxylate group of the quinaldinate ligand. The oxygen atom of the quinaldinate ligand is bonded *trans* to the nitrido ligand and the nitrogen atom is bonded in the equatorial plane, *trans* to one of the cyano ligands. The Mn=N bond distance of 1.523(5) Å is comparatively short. The two *trans* orientated cyano ligands have comparable Mn-C bond distances (see Table 6.3), but the Mn-C bond distance [1.984(5) Å] of the cyano ligand *trans* to the nitrogen atom of the quinaldinate ligand is slightly shorter. The Mn-C-N moieties are nearly linear with an average bond angle of 178.0(5)°. The Mn-N(11) bond distance is 2.110(4) Å and the Mn-O(11) bond distance is 2.168(4) Å. The long Mn-O(11) bond distance is an indication of the large *trans* influence of the nitrido ligand on the *trans*-bonded oxygen atom of the carboxylate group of the quinaldinate ligand.

The manganese bonded atoms in the $[\text{MnN}(\text{quin})(\text{CN})_3]^{2-}$ anion have a distorted octahedral geometry. The metal center of the $[\text{MnN}(\text{quin})(\text{CN})_3]^{2-}$ anion is displaced by 0.286(3) Å from the plane formed by the three cyano ligands and the nitrogen atom of the quinaldinate ligand towards the nitrido ligand. This displacement and the small bite angle of 76.4(2)° of the bidentate ligand cause considerable distortion of the coordination octahedron. The distortion is also evident from the deviation of the N(10)-Mn-C and C-Mn-O(11) bond angles from the ideal 90° for an octahedron, which ranged from 94.9(2)° to 97.3(2)° and 81.58(18)° to 84.88(18)° respectively. The distortion can be attributed to a strong π -bonded ligand such as an oxide or nitride ligand bonded in an axial position of an octahedral transition metal complex.

The bond distances and angles of the quinaldinate ligand in $[\text{MnN}(\text{quin})(\text{CN})_3]^{2-}$ are in good agreement with those found in $[\text{WO}(\text{pic})(\text{CN})_3]^{2-}$.³

6.5. $(\text{Ph}_4\text{As})_2[\text{MoO}(\text{pic})(\text{CN})_4]\cdot 3\text{H}_2\text{O}$

6.5.1. Introduction

The preparation of the $(\text{Ph}_4\text{As})_2[\text{MoO}(\text{pic})(\text{CN})_4]\cdot 3\text{H}_2\text{O}$ complex and the growth of the crystals used for collection of the intensity data were reported in § 3.3.16. A molecular diagram showing the numbering scheme of the anion is presented in Figure 6.3 and selected bond distances and angles are given in Table 6.4 with a discussion highlighting some of the important aspects of the $[\text{MoO}(\text{pic})(\text{CN})_3]^{2-}$ anion presented thereafter. A comparison with other relevant structures is given in § 6.6. Supplementary data containing complete lists of atomic coordinates, anisotropic displacement parameters, bond distances and angles as well as hydrogen coordinates are given in § A.10 in Appendix A.

The dark green crystals were quite stable over time and no loss of solvent molecules could be detected after a week. The complex crystallized in the triclinic space group, $\bar{P}1$, with two molecules per unit cell.

The crystal structure of $(\text{Ph}_4\text{As})_2[\text{MoO}(\text{pic})(\text{CN})_3]\cdot 3\text{H}_2\text{O}$ consisted of discrete $(\text{Ph}_4\text{As})^+$ cations and $[\text{MoO}(\text{pic})(\text{CN})_3]^{2-}$ anions. The geometry of the $(\text{Ph}_4\text{As})^+$ cations is tetrahedral with average As-C bond distances of 1.912(4) Å. The C-As-C bond angles range from 107.0(2)° to 111.7(2)° and the bond distances and angles of the carbon atoms in the phenyl rings are within normal limits. These bond distances and angles of the tetraphenylarsonium cations were within the normal limits found for previously determined structures containing this cation.^{3,9,10}

Short intermolecular contacts are formed between the water molecules of crystallization, the uncoordinated oxygen atom of the carboxylate group of the picolinate ligand and one of the nitrogen atoms of the cyano ligands [$\text{O}(3\text{W})\cdots\text{O}(12) = 2.49$ Å, $\text{O}(1\text{W})\cdots\text{N}(3) = 2.82$ Å, $\text{O}(1\text{W})\cdots\text{O}(2\text{W}) = 2.84$ Å, $\text{O}(2\text{W})\cdots\text{O}(3\text{W}) = 2.68$ Å]. The hydrogen atoms of the water molecules of crystallization were detected geometrically from the Fourier-difference map, but could not be refined satisfactorily.

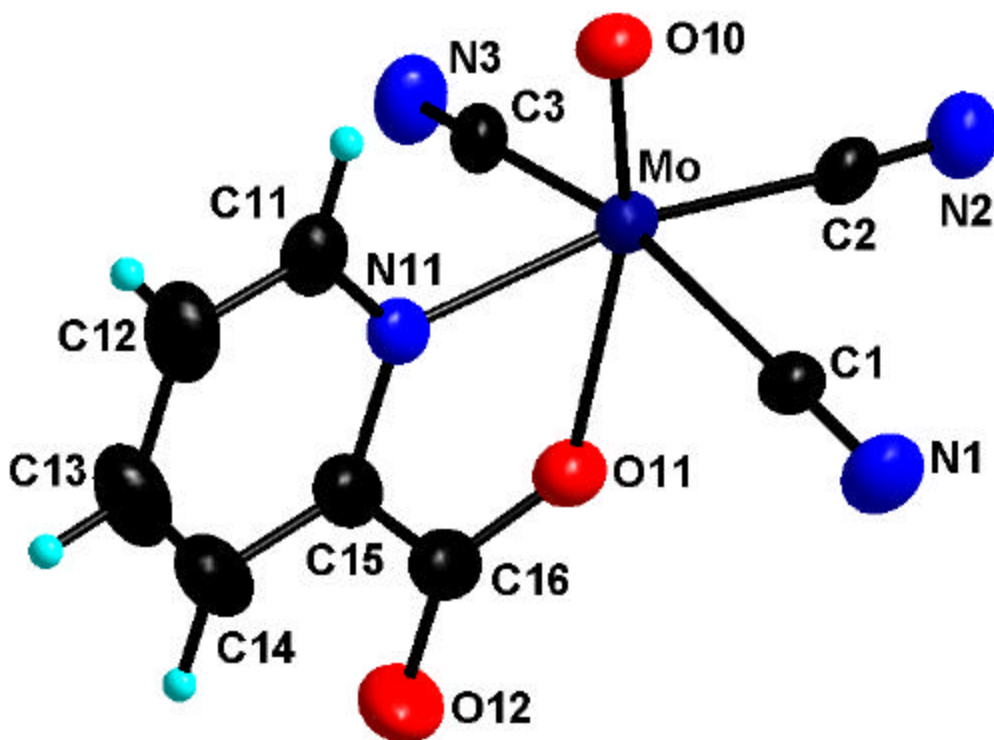


Figure 6.3: Molecular diagram showing the numbering scheme and displacement ellipsoids (30 % probability) of the $[\text{MoO}(\text{pic})(\text{CN})_3]^{2-}$ anion. The cations and solvent molecules are omitted for clarity.

Table 6.4 Selected bond lengths (Å) and angles (°) for the $[\text{MoO}(\text{pic})(\text{CN})_3]^{2-}$ anion.

Bond distances (Å)			
Mo-O(10)	1.681(3)	Mo-C(2)	2.125(6)
Mo-C(1)	2.165(5)	Mo-C(3)	2.177(5)
Mo-O(11)	2.191(3)	Mo-N(11)	2.216(4)
C(1)-N(1)	1.150(5)	C(2)-N(2)	1.147(6)
C(3)-N(3)	1.149(5)	N(11)-C(11)	1.336(6)
N(11)-C(15)	1.352(6)	C(11)-C(12)	1.369(7)
C(12)-C(13)	1.373(8)	C(13)-C(14)	1.377(8)
C(14)-C(15)	1.394(8)	C(15)-C(16)	1.495(8)
C(16)-O(12)	1.232(6)	C(16)-O(11)	1.263(6)
Bond angles (°)			
O(10)-Mo-C(2)	102.56(17)	O(10)-Mo-C(1)	100.36(15)
C(2)-Mo-C(1)	87.24(17)	O(10)-Mo-C(3)	100.47(15)
C(2)-Mo-C(3)	85.21(17)	C(1)-Mo-C(3)	158.93(17)
O(10)-Mo-O(11)	161.89(15)	C(2)-Mo-O(11)	95.55(16)
C(1)-Mo-O(11)	80.87(14)	C(3)-Mo-O(11)	80.33(14)
O(10)-Mo-N(11)	89.84(15)	C(2)-Mo-N(11)	167.57(16)
C(1)-Mo-N(11)	89.62(15)	C(3)-Mo-N(11)	93.55(15)
O(11)-Mo-N(11)	72.07(14)	N(1)-C(1)-Mo	175.6(4)
N(2)-C(2)-Mo	177.0(4)	N(3)-C(3)-Mo	174.7(4)
C(11)-N(11)-C(15)	118.4(5)	C(11)-N(11)-Mo	124.7(3)
C(15)-N(11)-Mo	116.8(4)	N(11)-C(11)-C(12)	123.1(5)
C(11)-C(12)-C(13)	119.0(6)	C(12)-C(13)-C(14)	119.1(6)
C(13)-C(14)-C(15)	119.3(6)	N(11)-C(15)-C(14)	121.0(5)
N(11)-C(15)-C(16)	114.8(5)	C(14)-C(15)-C(16)	124.1(5)
O(12)-C(16)-O(11)	125.4(6)	O(12)-C(16)-C(15)	120.0(6)
O(11)-C(16)-C(15)	114.6(5)	C(16)-O(11)-Mo	121.4(3)

6.5.2. Results and discussion

The molybdenum(IV) atom is octahedrally coordinated to an oxo ligand, three cyano ligands and the nitrogen atom of the aromatic ring as well as one of the oxygen atoms of the carboxylate group of the picolinate ligand. The nitrogen atom of the picolinate ligand was bonded *trans* to one of the equatorial cyano ligands and the oxygen atom was bonded *trans* to the oxo ligand. The two Mo-C bond distances [average = 2.171(5) Å] of the two *trans* bonded cyano ligands are similar, while the Mo-C bond distance [Mo-C(2) = 2.125(6) Å] of the cyano ligand bonded *trans* to the nitrogen atom of the picolinate ligand is much shorter compared to the same bond distances of the *trans* bonded cyano ligands. The Mo-O(10) bond distance is 1.681(3) Å and the Mo-O(11) bond distance is 2.191(3) Å. The lengthening of the Mo-C(11) bond distance can be attributed to the large *trans* influence of the oxo ligand compared to the oxygen atom of the carboxylate group.

The molybdenum-bonded atoms in the $[\text{MoO}(\text{pic})(\text{CN})_3]^{2-}$ anion have a distorted octahedral geometry with the metal center displaced by 0.309(2) Å from the plane formed by the three carbon atoms of the cyano ligands and the nitrogen atom of the picolinate ligand. This distortion coupled with the small bite angle of 72.1(1)° led to considerable distortion of the coordination octahedron. The deviation of the O(10)-Mo-C bond angles [range from 100.36(15)° to 102.56(17)°] as well as the C-Mo-O(11) bond angles [range from 80.33(14)° to 95.55(16)°] from the angular 90° for the ideal octahedron is also an indication of the mode of distortion of the coordination octahedron. As mentioned in the previous discussions this type of distortion can be attributed to a strong π -bonded ligand such as an oxide or nitride in an axial position of the coordination octahedron of transition metal complexes.

The bond distances and angles of the picolinate ligand in $[\text{MoO}(\text{pic})(\text{CN})_3]^{2-}$ are in good agreement with those found in $[\text{MnN}(\text{pic})(\text{CN})_3]^{2-}$ (see § 6.3.2) and $[\text{WO}(\text{pic})(\text{CN})_3]^{2-}$.³

6.6. Structural correlations of N,O-substituted nitrido complexes of manganese(V).

A summary of the average bond lengths, ligand bite angles and $\nu_{(M-X)}$ IR stretching frequencies for the N,O-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 6.5.

Table 6.5: Bond data for selected isoelectronic N,O-substituted cyano complexes of group 6 to 8 metal centers containing oxo or nitrido axial ligands.

Anion ^a	M=N or M=O	M-O ^b	D ^c	Bite angle	M-N ^d	M-C ^e	N(10)- M-O(11) angle	$\nu_{(MX)}$ ^f	Ref.
	(Å)	(Å)	(Å)	(°)	(Å)	(Å)	(°)	(cm^{-1})	
MnN(pic)	1.538(3)	2.214(3)	0.259(2)	76.1(1)	2.045(3)	1.931(5)	171.9(2)	1033	⁹
MnN(quin)	1.523(5)	2.168(4)	0.286(3)	76.4(2)	2.110(4)	1.984(5)	178.9(2)	1032	⁹
MoO(pic)	1.681(3)	2.216(4)	0.309(2)	72.1(1)	2.216(4)	2.125(6)	161.9(2)	944	⁹
WO(pic)	1.676(9)	2.171(8)	0.331(2)	72.5(4)	2.188(13)	2.042(18)	164.7(5)	944	³

^a MnN(pic) = [MnN(pic)(CN)₃]²⁻; MnN(quin) = [MnN(quin)(CN)₃]²⁻; MoO(pic) = [MoO(pic)(CN)₃]²⁻; WO(pic) = [WO(pic)(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

The crystal structure determinations of (Ph₄As)₂[MnN(pic)(CN)₃].4H₂O, (Ph₄As)₂[MoO(pic)(CN)₄].3H₂O and (Ph₄As)₂[WO(pic)(CN)₄].2H₂O³ have shown that these bidentate substitution products are isomorphous.

These are the first water soluble bidentate N,O-substituted complexes of the group 7 metal nitridotetracyano complexes characterized by X-ray crystallography. The

complexes were also crystallized as the tetraphenylarsonium salts (see § 4.7 and § 5.6). The structure determinations also showed that the entering bidentate ligand substituted the aqua ligand and one of the cyano ligands in the equatorial plane. As mentioned previously (§ 5.6), it is expected that the $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ complex is formed if the $(\text{Ph}_4\text{As})_2[\text{MnN}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ complex is dissolved in water due to the high concentration of the aqua ligand. It is also expected that the aqua ligand will be substituted first, since the $\text{M}-\text{OH}_2$ bond is much weaker than the $\text{M}-\text{CN}$ bond, especially in these complexes as a result of the large *trans* influence of the nitrido ligand. The second step in the two-step process is the ring-closure of the chelating ring with the simultaneous substitution of the cyano ligand. The crystal structure determinations (see Figure 6.1, Figure 6.2 and Figure 6.3) showed that the oxygen atom of the carboxylic acid group of the picolinate anion is bonded *trans* to the nitrido or oxo ligand in each case. This is interpreted as proof that the aqua ligand was indeed substituted first, since it is known that the oxygen atom in the types of bidentate ligands (such as the picolinate anion) will bond before the nitrogen atom of the pyridine ring. Kinetic results have shown that the monodentate substitution reactions^{11,12,13,14} of the tungsten complex are about 1000 times faster than those with bidentate ligands⁶ and the fact that the kinetic results also point to a dissociative mechanism, gives a strong indication that the substitution of the aqua ligand is a relatively fast reaction, whereas the substitution of the cyano ligand (ring closure) is relatively slow. Results from the kinetic study of the reaction of $[\text{WO}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ with the picolinate ligand⁶ have shown that the ring-closure step (substitution of the cyano ligand) is the rate-determining step. This is not surprising since the $\text{M}-\text{CN}$ bond is expected to be much stronger than the $\text{M}-\text{OH}_2$ bond.

The large *trans* influence of the nitrido ligand is also evident in the N,O-bidentate substituted complexes since the $\text{M}-\text{O}(11)$ bonds in these complexes are longer than expected (Table 6.5). The metal atom is displaced from the plane formed by the three carbon atoms of the cyano ligand and the nitrogen atom of the picolinate ligand. The distortion of the angles of the coordination octahedron is also proof of

¹¹ Leipoldt, J.G.; Basson, S.S.; Roodt, A.; Potgieter, I.M., *S. Afr. J. Chem.*, **1986**, 39, 179.

¹² Smit, J.P.; *Ph.D. thesis*, University of the Free State, Bloemfontein, South Africa, **1995**.

¹³ Leipoldt, J.G.; Van Eldik, R.; Basson, S.S.; Roodt, A., *Inorg. Chem.*, **1986**, 25, 4639.

¹⁴ Roodt, A.; Leipoldt, J.G.; Basson, S.S.; Potgieter, I.M., *Transition Met. Chem.*, **1988**, 13, 336.

this fact (see § 0, 6.4.2 and 0). 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 bite angles of the picolinate and quinaldinate ligands are similar within experimental error and this is expected due to the fact that the coordinating groups are bonded *via* the same carbon backbone in the ligand molecule (Table 6.5).

The IR stretching frequencies of the Mn=N bonds of the $[\text{MnN}(\text{pic})(\text{CN})_3]^{2-}$ and $[\text{MnN}(\text{quin})(\text{CN})_3]^{2-}$ complexes are very similar and this seems to indicate that the oxygen atoms of the carboxylate groups in these ligands have the same *trans* influences on the nitrido ligands. The Mn=N bond values for these complexes are very similar as well and thus support the observation of the *trans* influences of the oxygen atoms of these ligands. It seems that the extra aromaticity of the quinaldinate ligand (containing a naphthalene backbone) does not change the bonding capability of the pyridine nitrogen and the carboxylic oxygen atoms to a large extent compared to the pyridine nitrogen and carboxylic oxygen atoms of the picolinate ligand.

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 6.5 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 $\text{W}^{\text{IV}} = 0.66 \text{ \AA}$).¹⁵ This short bond distance can also be attributed to the charge on the manganese metal center (+5) compared to the molybdenum and tungsten (+4).

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

¹⁵ Shannon, R.D., *Acta Cryst.*, **1976**, A32, 751.

smaller ionic radius for the manganese(V) metal center than the molybdenum(IV) and tungsten(IV) metal centers (see Table 6.5).

The shorter M-C(2) bond distances compared to the M-C bond distances of the two *trans*-bonded cyano ligands can be explained in terms of the larger thermodynamic *trans* influence of the cyano ligand on a *trans* bonded ligand. The cyano ligand has a larger *trans* influence compared to the nitrogen atom of the picolinate ligand and this would lead to a shortening of the Mn-C(2) bond distance in contrast to the two other *trans* orientated cyano ligands with the longer Mn-C bond distances. The shorter M-C(2) bond distance can also be attributed to the fact that the nitrogen atom of the picolinate ligand has very weak or no π -bonding capability and this leads to extensive π -shortening of the Mn-C(2) bond. Thus, the degree of π -bonding has a large influence on the metal-carbon bond distances in cyano-complexes of group 6 to 8.

It was imperative to determine the crystal structures of these N,O-substituted nitrido complexes of manganese(V) since very little data is available on the bidentate substitution reactions of these nitrido complexes and the products thereof. Since the picolinate type of ligands have two different donor atoms, it was also important to determine if these ligands will have the same mode of bonding in the nitrido complexes as in the related oxo complexes. These structure determinations could also be helpful in the determination of the mechanism of these type of substitution reactions. Unfortunately, no crystals of the dipicolinate (like pyridine-2,3-dicarboxylic acid) were obtained even after numerous attempts and the use of a large variety of cations. However, the structure determinations clearly showed the coordination mode of the bidentate ligand and will be used in the following chapter to assist in deriving a reaction mechanism for the bidentate substitution reactions of the $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ complex (see Chapter 7).