
3. Synthesis and Characterization of the Complexes

3.1 Introduction

The syntheses and spectroscopic characterization of the complexes prepared during this study are discussed in this chapter. Several of the complexes described were also characterized by means of X-ray crystallography and will be discussed in more detail in Chapter 4, 5 and 6. Correlation between crystallographic studies and the IR data reported in this chapter will also be discussed in more detail in the above-mentioned chapters.

It is somewhat surprising that the research into the nitridotetracyano complexes of manganese(V)^{1,2} has not received much attention up to date, whereas the corresponding analogues of technetium(V), rhenium(V) and osmium(VI) are known. Thus, $[\text{TcN}(\text{OH}_2)(\text{CN})_4]^{2-}$,³ $[\text{ReN}(\text{OH}_2)(\text{CN})_4]^{2-}$,⁴ $[\text{ReN}(\text{CN})_5]^{3-}$,⁵ $[\text{ReN}(\text{N}_3)(\text{CN})_4]^{3-}$ ⁶ and $[\text{OsN}(\text{OH})(\text{CN})_4]^{2-}$ ⁷ have been synthesized and the tetraphenylphosphonium or tetraphenylarsonium salts of these anions have been crystallographically characterized.

Fairly simple synthetic routes are available for the synthesis of the nitridotetracyano complexes of technetium(V), rhenium(V) and osmium(VI). It seems that only a limited number of synthetic routes are available for the synthesis of the nitridotetracyano complexes of manganese(V). The most widely used method is the

¹ Bendix, J.; Meyer, K.; Weyhermüller, T.; Bill, E.; Metzler-Nolte, N.; Wieghardt, K., *Inorg. Chem.*, **1998**, 37, 1767.

² Bendix, J.; Deeth, R.J.; Weyhermüller, T.; Bill, E.; Wieghardt, K., *Inorg. Chem.*, **2000**, 39, 930.

³ Baldas, J.; Boas, J.F.; Colmanet, S.F.; Mackay, M.F., *Inorg. Chim. Acta*, **1990**, 170, 233.

⁴ Purcell W.; Potgieter I. M.; Damoense L. J.; Leipoldt J. G., *Transition Met. Chem.*, **1992**, 17, 387.

⁵ Purcell, W.; Potgieter, I.M.; Damoense, L.J.; Leipoldt, J.G., *Transition Met. Chem.*, **1991**, 16, 473.

⁶ Purcell, W.; Damoense, L.J.; Leipoldt, J.G., *Inorg. Chim. Acta*, **1992**, 195, 217.

⁷ Van der Westhuizen, H.J.; Basson, S.S.; Purcell, W., *Transition Met. Chem.*, **1994**, 19, 582.

photolysis of azido manganese(III) precursors (Arshankov reaction).⁸ The treatment of manganese(III) porphinato and N,N'-ethylenebis(salicylidene-aminato) (salen) complexes with either NaOCl or PhIO in the presence of aqueous ammonia also yields the $Mn^V=N$ species.^{9,10,11} The nitridophthalocyaninato complexes of manganese(V) have been obtained from the oxidation of $[Mn^{III}(OH)Pc(2-)]$ in aqueous NH_3 solution with chlorine. More recently, an efficient synthesis of $Mn^V=N$ complexes containing Schiff base ligands *via* oxidation of manganese(III) precursors in CH_2Cl_2/NH_3 solution with N-bromosuccinimide (NBS) was reported.¹² It was discovered the nitridotetracyano complexes of manganese(V) are readily synthesized by ligand substitution of the salen ligand of $[Mn^V N(salen)]$ by CN^- in aqueous solutions of NaCN.¹

All complexes containing a $Mn^V=N$ structural moiety are, with one notable exception,¹³ five-coordinate with a square based pyramidal coordination polyhedron with the nitrido ligand in the apical position. The coligands employed are usually four coordinate porphinato(2-), phthalocyaninato(2-) or NN'-ethylenebis(salicylideneaminato)(2-) derivatives or two Schiff base ligands.¹⁴ These ligands display strong charge-transfer bands in the visible region, and consequently, d-d transitions arising from the d^2 electron configuration have not been readily identified or assigned.

3.2 Chemicals and instrumentation

Caution! Cyanide compounds are extremely toxic and HCN can be generated under certain conditions while working with these compounds. Therefore, the appropriate care was taken as far as possible and all manipulations of the complexes were done in an efficient fume hood.

⁸ Arshankov, S.I.; Poznjak, A.L., *Z. Anorg. Allg. Chem.*, **1981**, 481, 201.

⁹ Buchler, J.W.; Dreher, C.; Lay, K.-L., *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **1982**, 37B, 1155.

¹⁰ Hill, C.L.; Hollander, F.J., *J. Am. Chem. Soc.*, **1982**, 104, 7318.

¹¹ Buchler, J.W.; Dreher, C.; Lay, K.-L.; Lee, Y.J.A.; Scheidt, W.R., *Inorg. Chem.*, **1983**, 22, 888.

¹² Du Bois, J.; Tomooka, C.S.; Hong, J.; Carreira, E.M.; Day, M.W., *Angew. Chem., Int. Ed. Engl.*, **1997**, 36, 1645.

¹³ Niemann, A.; Bossek, U.; Haselhorst, G.; Wieghardt, K.; Nuber, B., *Inorg. Chem.*, **1996**, 35, 906.

¹⁴ Du Bois, J.; Tomooka, C.S.; Hong, J.; Carreira, E.M., *Acc. Chem. Res.*, **1997**, 30, 364.

All the chemicals used during the syntheses of the complexes were obtained from Merck or Sigma-Aldrich Chemical Company and used without further purification. Double distilled water was used in the syntheses and all the syntheses were performed in the open air. The UV/vis spectra were recorded on Varian Cary 50 Conc or Varian 100 spectrophotometers using 1.000 ± 0.001 cm quartz cells. All infrared spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer and analysed with the Bruker OPUS-NT software. The NMR spectra were recorded on a Varian Gemini 2000 300 MHz spectrometer (^1H : 300 MHz) at ambient temperature. The NMR spectra were recorded in CDCl_3 or D_2O and the ^1H spectra were calibrated relative to the residual CHCl_3 (7.24 ppm) or H_2O (4.60 ppm) peak as applicable.

3.3 Synthesis of the different complexes and compounds

3.3.1 2,2'-[1,2-ethanediylbis(nitrilomethylidene)]diphenol $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$ (H_2salen)

This compound was prepared as described previously and was used without further purification.¹⁵

3.3.2 $[\text{MnN}(\text{salen})]^{1+}$ (335.24 g mol⁻¹)

N,N-bis(salicylaldehydeethylenediimine) (salen) (8.1 g, 0.030 mmol) was dissolved in methanol (400 cm³) and heated to 50 - 60 °C. Manganese(II) acetate (5.45 g, 31.5 mmol) was added to the salen solution in small portions and the reaction mixture was heated under reflux for 1 hour. The dark brown solution was cooled and stirred at room temperature for 30 minutes. Concentrated ammonia solution (13 M, 36 cm³, 465 mmol, 15 equivalents) was added drop-wise to the dark brown solution over a 5 minute period. A concentrated solution of sodium hypochlorite (0.47 M, 420 cm³, 196 mmol, 6 equivalents) was added drop-wise over 40 minutes, while the solution was

¹⁵ Mason, A.T., *Chem. Ber.*, **1887**, 20, 271.

stirred vigorously. The reaction mixture was cooled on an ice bath and filtered to remove the black-green precipitate. The precipitate was extracted with CH_2Cl_2 until the colour of the solvent remained faint green. The CH_2Cl_2 was removed *in vacuo* to leave the black green residue of $[\text{MnN}(\text{salen})]$ in the flask.

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1047 \text{ cm}^{-1}$.

3.3.3 $[(\text{CH}_3)_4\text{N}]_2\text{Na}[\text{MnN}(\text{CN})_5]\cdot\text{H}_2\text{O}^1$ (388.33 g mol⁻¹)

$[(\text{CH}_3)_4\text{N}]_2\text{Na}[\text{MnN}(\text{CN})_5]\cdot\text{H}_2\text{O}$ was prepared with a slight modification to the published procedure.¹ $[\text{MnN}(\text{salen})]$ (5.0 g, 15 mmol) was suspended in water (250 cm³) and methanol (50 cm³). Sodium cyanide (22.0 g, 449 mmol) was added and the suspension was heated under reflux for 8 hours or until no $[\text{MnN}(\text{salen})]$ could be detected in the solution. The red-brown solution was filtered while it was still hot and tetramethylammonium chloride (36.0 g, 328 mmol) was added to the hot solution. Methanol (100 cm³) was then added to this solution and the solution cooled to $\sim 5 \text{ }^\circ\text{C}$ overnight. The pink product was filtered and washed three times with methanol (20 cm³). Yield: 5.73 g (99 %).

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1003 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{N})} = 2118 \text{ cm}^{-1}$ (see Figure 3.1).

3.3.4 $(\text{Ph}_4\text{As})_2[\text{MnN}(\text{CN})_4]\cdot 2\text{H}_2\text{O}^1$ (975.75 g mol⁻¹)

$[(\text{CH}_3)_4\text{N}]_2\text{Na}[\text{MnN}(\text{CN})_5]\cdot\text{H}_2\text{O}$ (1.60 g, 4.12 mmol) and NaCN (0.60 g, 12.4 mmol) were dissolved in a minimum amount of water ($\sim 45 \text{ cm}^3$). Tetraphenylarsonium chloride (3.6 g, 8.24 mmol) was dissolved in water (50 cm³) and added to the above-mentioned solution, whilst the solution was stirred. The product precipitated immediately as orange-pink needles. The solution was stirred for 1 hour and the orange-pink product was filtered. Yield: 2.89 g (72 %).

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1105 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{N})} = 2114 \text{ cm}^{-1}$.

3.3.5 (Ph₄P)₂[MnN(CN)₄]-2H₂O¹ (887.86 g mol⁻¹)

[(CH₃)₄N]₂Na[MnN(CN)₅]-H₂O (1.65 g, 4.25 mmol) and NaCN (0.60 g, 12.2 mmol) were dissolved in a minimum amount of water (± 45 cm³). Tetraphenylphosphonium chloride (3.6 g, 9.60 mmol) was dissolved in water (60 cm³) and added to the above-mentioned solution. The product precipitated immediately as orange-pink needles. The solution was stirred for 1 hour and the orange-pink product was filtered. Yield: 3.28 g (87 %).

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1105$ cm⁻¹, $\nu_{(\text{C}=\text{N})} = 2114$ cm⁻¹ (see Figure 3.1).

3.3.6 [Rh(en)₃][MnN(OH)(CN)₄] (473.23 g mol⁻¹)

[(CH₃)₄N]₂Na[MnN(CN)₅]-H₂O (0.075 g, 0.19 mmol) was dissolved in a 1M NaOH solution (2 cm³). [Rh(en)₃]Cl₃-3H₂O (0.130 g, 0.29 mmol) was dissolved in a 1M NaOH solution (1.5 cm³) and added to the above-mentioned solution. This solution was filtered and covered with laboratory film with a few small holes in it. It was left at ambient temperature and purple crystals were obtained after ca. 4 days. Yield: 0.085 g (95 %).

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1002$ cm⁻¹, $\nu_{(\text{C}=\text{N})} = 2117$ cm⁻¹ (see Figure 3.2).

3.3.7 [Rh(en)₃][MnN(NCS)(CN)₄]-H₂O (532.25 g mol⁻¹)

[(CH₃)₄N]₂Na[MnN(CN)₅]-H₂O (0.06 g, 0.15 mmol) was dissolved in a 1M NaSCN solution (2 cm³). [Rh(en)₃]Cl₃-3H₂O (0.120 g, 0.27 mmol) was dissolved in a 1M NaSCN solution (1.5 cm³) and added to the above-mentioned solution. This solution was filtered and covered with laboratory film with a few small holes in it. It was left at ambient temperature and red crystals were obtained after ca. 3 days. The crystals were suitable for the Xray crystal structure determination of this compound. Yield: 0.0729 g (89 %).

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1056$ cm⁻¹, $\nu_{(\text{C}=\text{N}, \text{NCS}^-)} = 2068$ cm⁻¹, $\nu_{(\text{C}=\text{N})} = 2126$ cm⁻¹, $\nu_{(\text{CS})} = 874$ cm⁻¹ (see Figure 3.2).

3.3.8 [Rh(en)₃][MnN(N₃)(CN)₄] (498.17 g mol⁻¹)

[(CH₃)₄N]₂Na[MnN(CN)₅]·H₂O (0.06 g, 0.15 mmol) was dissolved in a 1M NaN₃ solution (2 cm³). [Rh(en)₃]Cl₃·3H₂O (0.120 g, 0.27 mmol) was dissolved in a 1M NaN₃ solution (1.5 cm³) and added to the abovementioned solution. This solution was filtered and covered with laboratory film with a few small holes in it. It was left at ambient temperature and orange crystals were obtained after ca. 2 days. Yield: 0.0709 g (92 %).

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1057 \text{ cm}^{-1}$, $\nu_{(\text{N}=\text{N}, \text{N}_3^-)} = 2043 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{N})} = 2125 \text{ cm}^{-1}$ (see Figure 3.2).

3.3.9 (Ph₄P)₂[MnN(3-pic)(CN)₄]-3-pic (1038.02 g mol⁻¹)

(Ph₄P)₂[MnN(CN)₄]·2H₂O (0.060 g, 0.068 mmol) was dissolved in methanol (~1 cm³) and 3-methylpyridine (3 cm³) was added to this solution. The solution was allowed to evaporate at ambient temperature in a fume hood and pink needles formed. The crystals were obtained after 2 days and they were suitable for the X-ray structure determination of this compound. Quantitative yield.

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1040 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{N})} = 2114 \text{ cm}^{-1}$ (see Figure 3.1).

¹H NMR (CDCl₃): δ 8.42 (t, 1H); δ 7.92-7.59 (m, 40H); δ 7.48 (d, 1H); δ 7.17 (dd, 1H); δ 2.33 (s, 3H).

3.3.10 (Ph₄P)₂[MnN(4-pic)(CN)₄]-0.5(4-pic)-H₂O (1009.47 g mol⁻¹)

This compound was synthesized analogous to (Ph₄P)₂[MnN(3-pic)(CN)₄]-3-pic, using 4-methylpyridine instead of 3-methylpyridine. Red crystals were obtained after two days and they were suitable for the X-ray analysis of this compound. Quantitative yield.

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1043 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{N})} = 2127 \text{ cm}^{-1}$ (see Figure 3.1).

¹H NMR (CDCl₃): δ 8.46 (d, 2H); δ 7.92-7.59 (m, 40H); δ 7.10 (d, 2H); δ 2.35 (s, 3H).

3.3.11 (Ph₄As)[MnN(en)(CN)₃] (590.43 g mol⁻¹)

(Ph₄As)₂[MnN(CN)₄]·2H₂O (0.150 g, 0.15 mmol) was dissolved in neat 1,2-diaminoethane. (C₆H₅)₄AsCl (0.10 g, 0.23 mmol) was added to the solution and it was left at ambient temperature in a desiccator to evaporate. Blue-purple crystals were obtained after ca. 1 week and were used for the X-ray analysis of this compound. Yield: 0.045 g (51 %).

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1022 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{N})} = 2113 \text{ cm}^{-1}$ (see Figure 3.3).

¹H NMR (CDCl₃): $\delta 7.90\text{-}7.63$ (m, 40H).

3.3.12 (Ph₄P)[MnN(bipy)(CN)₃]·0.5(bipy)·2H₂O (756.69 g mol⁻¹)

(Ph₄P)₂[MnN(CN)₄]·2H₂O (0.075 g, 0.084 mmol) and 2,2'-bipyridyl (0.10 g, 0.64 mmol) were dissolved in ethanol (15 cm³). Water (25 cm³) was added to the solution and it was heated at 70 °C for 5 hours. A water-ethanol mixture (1:2) was added periodically during the heating period to keep the total volume of the solution at 40 cm³. The solution was allowed to evaporate to about 10 cm³ near the end of the heating period, after which it was cooled to room temperature and filtered. Dark red crystals were obtained after ca. 1 day and they were used for the X-ray structure determination of this compound. Yield: 0.0603 g (94 %).

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1027 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{N})} = 2120 \text{ cm}^{-1}$ (see Figure 3.3).

¹H NMR (CDCl₃): $\delta 8.67$ (d, 2H); $\delta 8.43$ (d, 2H); $\delta 7.92\text{-}7.59$ (m, 40H); $\delta 7.38$ (t, 2H).

3.3.13 (Ph₄P)[MnN(phen)(CN)₄] (666.58 g mol⁻¹)

(Ph₄P)₂[MnN(CN)₄]·2H₂O (0.150 g, 0.17 mmol) and 1,10-phenantroline (0.240 g, 1.21 mmol) were dissolved in ethanol (15 cm³). Water (25 cm³) was added to the solution and it was heated at 70 °C for 5 hours. A water-ethanol mixture (2:1) was added periodically during this period to keep the total volume of the solution at 40 cm³. The solution was allowed to evaporate to about 10 cm³ near the end of the heating

period, after which it was cooled to room temperature and filtered. Dark red crystals were obtained after *ca.* 1 day and the crystals were also suitable for the X-ray analysis of this compound. Yield: 0.107 g (95 %).

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1024 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{N})} = 2118 \text{ cm}^{-1}$ (see Figure 3.3).

^1H NMR (CDCl_3): δ 8.28 (d, 2H); δ 7.98-7.65 (m, 40H); δ 7.62 (dd, 2H).

3.3.14 $(\text{Ph}_4\text{As})_2[\text{MnN}(\text{pic})(\text{CN})_4]\cdot 4\text{H}_2\text{O}$ (1107.82 g mol $^{-1}$)

$(\text{Ph}_4\text{As})_2[\text{MnN}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ (0.20 g, 0.20 mmol) was dissolved in ethanol (10 cm 3). Sodium pyridine-2-carboxylate (0.44 g, 3.03 mmol) was dissolved in water (20 cm 3) and added to the $[\text{MnN}(\text{CN})_4]^{2-}$ solution. The solution was heated at 70 °C for 8 hours. The total volume of the solution was kept at *ca.* 20 cm 3 and was reduced to *ca.* 5 cm 3 near the end of the 8 hours. The solution was filtered and dark red crystals formed after 2 days, which were filtered off. These crystals were used for the X-ray structure determination of this compound. Yield: 0.200 g (90 %).

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1033 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{N})} = 2124 \text{ cm}^{-1}$ (see Figure 3.4).

UV/Vis: UV/Vis: λ_{max} , 372, 520 nm; ϵ , 2161.2, 105.8 l mol $^{-1}$ cm $^{-1}$.

^1H NMR (CDCl_3): δ 7.87-7.55 (m, phenyl-H).

3.3.15 $(\text{Ph}_4\text{As})_2[\text{MnN}(\text{quin})(\text{CN})_3]\cdot 3\text{H}_2\text{O}$ (1139.86 g mol $^{-1}$)

$(\text{Ph}_4\text{As})_2[\text{MnN}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ (0.150 g, 0.153 mmol) was dissolved in methanol (10 cm 3). Sodium quinaldinate (0.20 g, 1.02 mmol) was dissolved in water (20 cm 3) and added to the $[\text{MnN}(\text{CN})_4]^{2-}$ solution. The solution was heated at 60 °C for 8 hours and the total volume of the solution was kept at *ca.* 15 cm 3 . After filtering the solvent was allowed to evaporate at ambient temperature. Dark red crystals were obtained after *ca.* 3 days and these crystals were used for the X-ray analysis of this compound. Yield: 0.157 g (90 %).

Spectral data: IR (KBr): $\nu_{(\text{Mn}=\text{N})} = 1032 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{N})} = 2116 \text{ cm}^{-1}$ (see Figure 3.4).

^1H NMR (CDCl_3): δ 7.87-7.55 (m, phenyl-H).

3.3.16 (Ph₄As)₂[MoO(pic)(CN)₃]₂·3H₂O (1132.79 g mol⁻¹)

K₃Na[MoO₂(CN)₄]₂·H₂O was prepared according to the published method.¹⁶ A sodium carbonate buffer solution (0.1 M) was prepared and the pH of this solution was adjusted to 10. K₃Na[MoO₂(CN)₄]₂·H₂O (0.10 g, 0.21 mmol) and sodium picolinate (0.21 g, 1.45 mmol) were dissolved in 10 cm³ of the buffer solution. The colour of the solution changed from blue to dark green. Ph₄AsCl (0.017 g, 0.04 mmol) was dissolved in 2 cm³ of the buffer solution and added to the above-mentioned reaction mixture. Dark green crystals formed overnight and were suitable for the X-ray structure determination of this compound. Yield: 0.0167 g (38 %).

Spectral data: IR (KBr): $\nu_{(\text{Mo}=\text{O})} = 944 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{N})} = 2091 \text{ cm}^{-1}$ (see Figure 3.4).

UV/Vis: λ_{max} , 418, 628 nm; ϵ , 2943, 362.1 M⁻¹ cm⁻¹.

¹H NMR (CDCl₃): δ 7.90-7.64 (m, phenyl-H).

3.3.17 [Rh(en)₃]Cl₃·3H₂O (443.61 g mol⁻¹)

This compound was synthesized and characterized according to the published procedure.¹⁷

¹⁶ Basson, S.S.; Leipoldt, J.G.; Potgieter, I.M., *Inorg. Chim. Acta*, **1984**, 87, 71.

¹⁷ Galsbøl, F., *Inorg. Synth.*, **1969**, 12, 269.

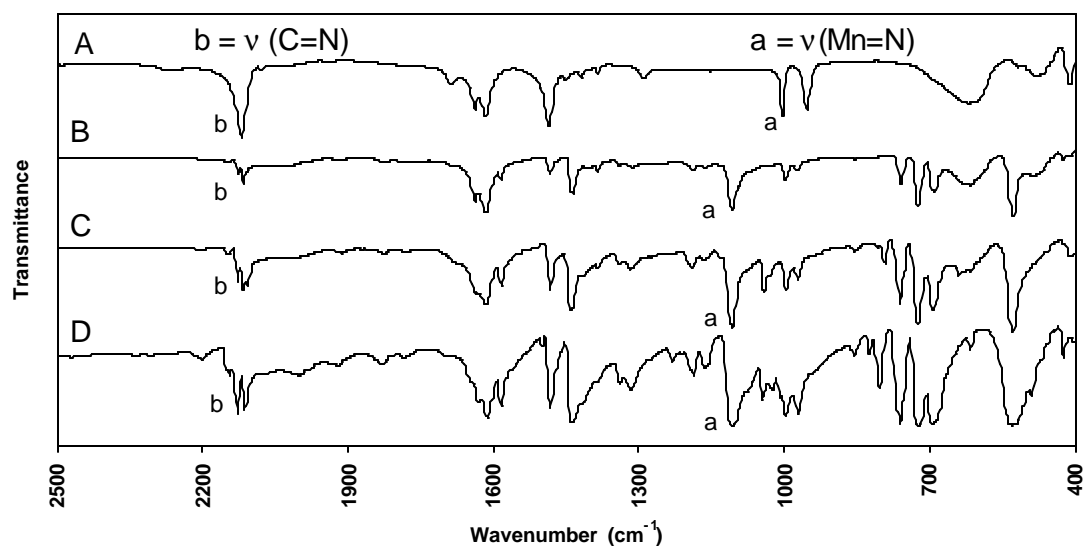


Figure 3.1: Infrared spectra of $[(\text{CH}_3)_4\text{N}]_2\text{Na}[\text{MnN}(\text{CN})_5]\cdot\text{H}_2\text{O}$ (A), $(\text{Ph}_4\text{P})_2[\text{MnN}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ (B), $(\text{Ph}_4\text{P})_2[\text{MnN}(3\text{-pic})(\text{CN})_4]\cdot 3\text{-pic}$ (C) and $(\text{Ph}_4\text{P})_2[\text{MnN}(4\text{-pic})(\text{CN})_4]\cdot 0.5(4\text{-pic})\cdot\text{H}_2\text{O}$ (D) (KBr disks).

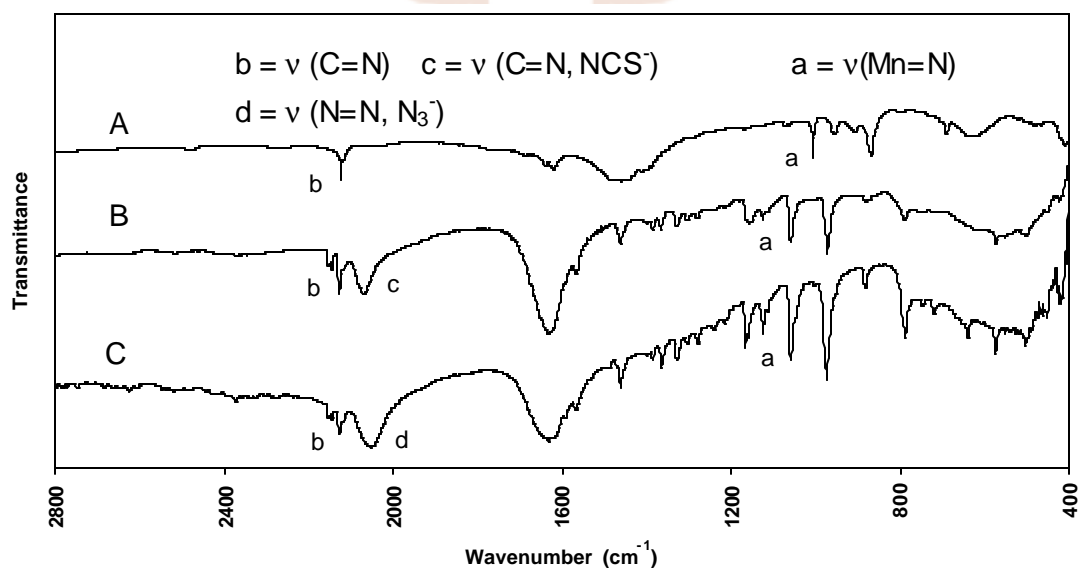


Figure 3.2: Infrared spectra of the monodentate substituted nitrido complexes of manganese(V), $[\text{Rh}(\text{en})_3][\text{MnN}(\text{OH})(\text{CN})_4]$ (A), $[\text{Rh}(\text{en})_3][\text{MnN}(\text{NCS})(\text{CN})_4]\cdot\text{H}_2\text{O}$ (B) and $[\text{Rh}(\text{en})_3][\text{MnN}(\text{N}_3)(\text{CN})_4]$ (C) (KBr disks).

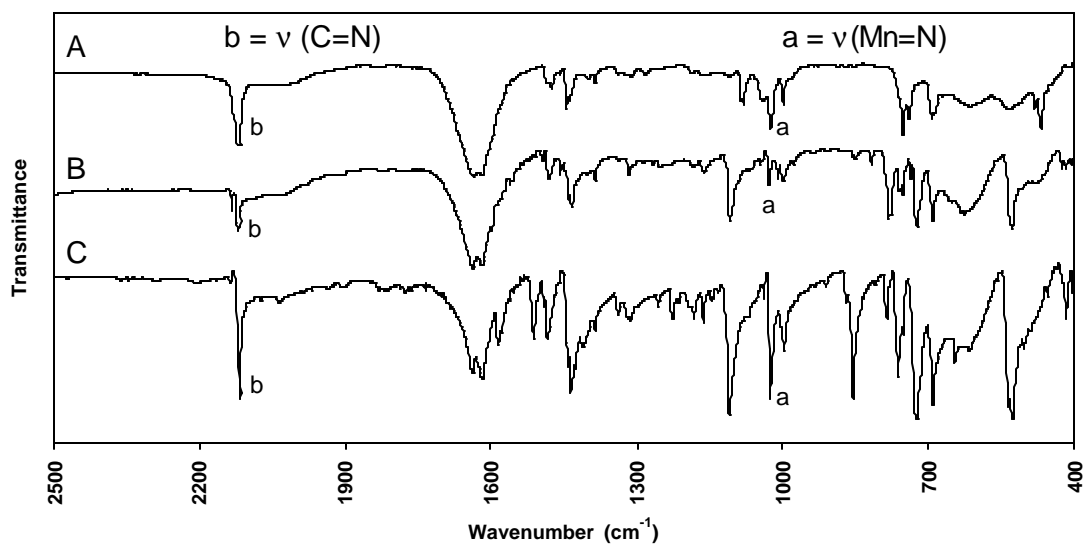


Figure 3.3: Infrared spectra of the N,N'-substituted nitrido complexes of manganese(V), (Ph₄As)[MnN(en)(CN)₃] (A), (Ph₄P)[MnN(bipy)(CN)₃]·0.5(bipy)·2H₂O (B), (Ph₄P)₂[MnN(phen)(CN)₄] (C) (KBr disks).

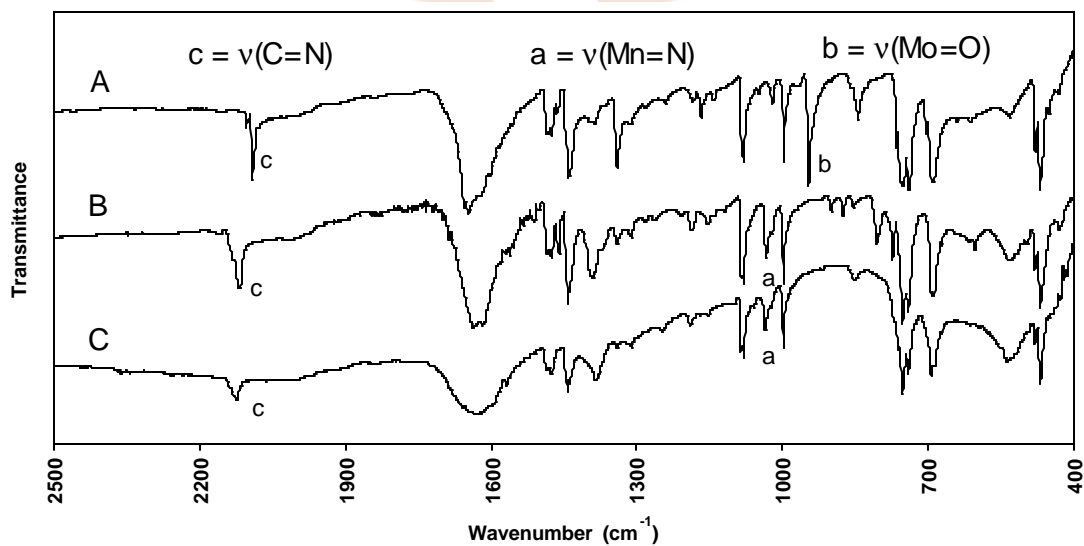


Figure 3.4: Infrared spectra of the N,O-substituted nitrido complexes of manganese(V), (Ph₄As)₂[MoO(pic)(CN)₃]·3H₂O (A), (Ph₄As)₂[MnN(quin)(CN)₃]·3H₂O (B), (Ph₄As)₂[MnN(pic)(CN)₄]·4H₂O (C) (KBr disks).