1,10-PHENANTHROLINE AND 4,4'-BIPYRIDINE COMPLEXES OF MANGANESE (II) TETRAFLUOROBORATE

K.S. PATEL, J.T. AYODELE+ and A.I. IHUARULAM
Department of Chemistry, Bayero University, P.M.B 3011 Kano, Nigeria.

(*Submitted*: 30 March 2004; *Accepted*: 30 October 2004)

Abstract

The synthesis of the complexes of manganese (II) tetrafluoroborate with 1,10-phenanthroline and 4,4'-bipyridine have been carried out. Elemental analysis, molar conductivity, magnetic properties and infrared (IR) spectral studies were used in characterizing these compounds. Octahedral geometry has been proposed where the ligands behave as bidendates coordinating through the amine.

1. Introduction

Tetrafluoroborate ion [BF_4^-] is a strong acidic anion such that its conjugate acid tetrafluoroboric acid HBF_4 is strong (Hathenway *et al.*, 1962). The BF_4 anion interacts with transition metal cations in non-aqueous solvents of relatively low permittivity but decomposes on the removal of the solvents (Kalo *et al.*, 1964). It however shows limited decomposition in water (Dillard and Goldberg, 1978). 1,10-Phenanthroline, a tricyclic heterocyclic compound with two pyridine nuclei fused to a benzene ring, is weakly basic with a pk value of 4.5-5.0 (Buckingham,1982; Scagliarini and Cosari,1964). Although it has two potentially basic nitrogen atoms per molecule, it is a mono protic base because of the stearic factor precluding the admission of a second hydrogen atom (Scagliarini and Cosari, 1964). It forms complexes with ferrous and other metallic ions through the nitrogen atoms to the same metal ions as a potential bidendates ligand (Kazybaev *et al.*, 1972). 4, 4'-bipyridine contains two pyridine nuclei joined together through a bond at the 4- and 4'-positions. Although there are two N basic atoms per molecule, the structure precludes chelation favouring co-ordination of the nitrogen atoms to two different metal ions. It coordinates to form polymeric complexes that are regarded as bidentate ligands (Musgrave and Mattson, 1968).

1,10-Phenanthroline has found useful applications. It is a biologically active compound. It is a useful inhibitor in microbial degradation of cholesterol (Nagasawa *et al.*, 1970) and as a coenzyme competitive inhibitor in horse-liver (Young *et al.*, 1971). It plays some important roles in the production of beans (Sleer and Gibbs, 1969) and is used in the quantitative analysis of metals and non-metals (Crowell and Kong, 1968; Sleer and Gibbs, 1969; Nagasawa *et al.*, 1970; Young *et al.*, 1971; Cole, 1973). 4, 4'- bipyridine is efficient in linking different units which play important part in the aerobic oxidation of cytochrome C (Smith, 1924), as an herbicide, its quarter nary salts have been useful in the control and eradication of harmful micro-organisms (Peard and Flaun, 1958; Lever *et al.*, 1964).

It serves as an inhibitor against corrosion of metals (Raa *et al.*, 1970) while its alcoholic solution prevents the corrosion of brass, solder, copper, aluminum and iron (Elder, 1969). The potential biological and industrial applications of 1,10-phenanthroline and 4, 4'-bipyridine complexes have been reported (Horold and Warren, 1981). Their metal complexes also have potential biological and industrial applications which include mimicking restriction of enzymes sites on DNA (Horold and Warren, 1981), inhibition of the hydrogenase activity by interfering with the electron carrier in vine extract (Laptowski and Muecyslalw, 1980), as protective coating and fast drier in paint and related products (Laptowski and Muecyslalw, 1980), detection of hexacyanoferrates (Yean, 1983), slowing down the rates of enzyme reactions (Sigel, 1986), anaerobic oxidation of cytochrome C (Smith,1924), as herbicide and in the control and eradication of harmful microorganisms (Peard and Flaun, 1958; Lever *et al.*, 1964), in the polarographic determination of cadmium and the spectrophotometric determination of nickel and copper in aluminum alloys (Smith, 1924; Lever *et al.*, 1964; Fielden and Summers, 1974; Helmont, 1986).

4, 4'-bipyridine metal complexes are used in studying the functions of some enzymes as they slow down their rate of reaction (Sigel, 1986). They are used in

+ corresponding author (email: tjayodele@yahoo.com)

the polarographic determination of micro amounts of cadmium in nickel based alloy and in waste water (Xiangym and Zhengzhong, 1985).

This paper reports the synthesis of 1,10-Phenanthroline and 4, 4'- bipyridine complexes of manganese (II) tetrafluoroborate.

2. Materials and Methods

In the preparation of ligands and complexes, chemicals of analytical grade purity and distilled water were used. All glass and plastic wares were washed with detergent and rinsed with distilled water before drying. All weightings were carried out on a Mettler balance H_{30}. All melting point determinations were carried out employing Gallen-Kamp melting point apparatus and a 0-360° C thermometer. Electrical measurements were determined using a conductivity measuring set model 4010. Infrared studies were recorded on a Fourier transformed IR (FTI) model attached to IBM compatible data station with laser jet printer in the region 4000-450 cm^{-1} and a Beckman spectrophotometer in the spectral region of 4000-650 cm^{-1}.

(a) Preparation of the ligands
The ligands 1,10-Phenanthroline and 4,4'-bipyridine were prepared as previously described (Yanorski and Sutzhanov, 1970). The infrared spectra of the ligands were characterized by absorption bands at the following frequencies 1645 s, 1618 w, 1590 w, 1450 s, 1427 s, 1410 w, 1375 sh, 1340 s, 1247 m 962 m, 908 m, 884 w, 855 w, 797 w,7305 s for 1,10-Phenanthroline (Schilt and Taylor, 1959; Inskeep, 1962) while those of 4,4'-bipyridine were characterized by the absorption bands at the following frequencies (cm^{-1}) 1580 s, 893 s,750 s, and 815 s (Dimroth and Frister, 1921; Hatton and Henene, 1921; Keat and Summers, 1976).

(b) Preparation of Mn (II) $(BF_4)_2.6H_2O$
To 50cm^3 of 1:1 tetrafluoroboric acid/water mixture in a 250cm^3 beaker was added excess manganese carbonate with stirring until effervescence ceased. The mixture was filtered and the filtrate was concentrated by heating on a hot plate and was left in a desiccator over silica gel to a white crystalline product with a yield of 53%. EDTA was used as a complexing agent using murexide as indicator (Pologikh *et al*., 1975). Found (Mn 16.32%, cal (15.43%) determined manganese Mn 18.42 for Mn $(BF_4)_2 6H_2O$.

(c) Preparation of 1,10-Phenanthroline Mn (II) $(BF_4)_2.6H_2O$.
3.604 g (0.01 mol) Mn(II) $(BF_4)_2$ $5H_2O$ and 1.188 g (0.03 mol) 1,10-Phenanthroline were reacted in 80 cm^3 water-ethanol mixture in a 250 cm^3 quick fit conical flask. The dirty white precipitate formed was filtered, washed several times with ethanol and was dried over silica get in a desiccator. The white crystalline complex decomposed at 137-138 °C.

(d) 4,4'-bipyridine cobalt (II) tetrafluoroborate.
40 cm^3 of 0.1M Mn $(BF_4)_2.6H_20$ was reacted with 80 cm^3 of 0.4M $C_{10}H_8N_2$ in 250 cm^3 conical flask and was stirred. The white precipitate formed was filtered and was washed with ethanol/water mixture. The white crystalline product was dried in the oven at 80 °C. Manganese in the complexes was estimated by EDTA titration after digesting the complexes with conc. $HN0_3$. The micro analytical laboratory at the University of Leeds UK performed elemental analyses for C, H, and N. The analytical data are presented in Table 1.

3. Results and Discussion

The formation of the complexes can be represented by the general equation:

$$M(BF_4)_2.6H_2O + xL \rightarrow [M (L)_X] (BF_4)_2.6H_2O$$

where: *L* = 1, 10-Phenanthroline and 4,4'-bipyridine; X = 1, 2, 3.

The complexes were blue powders with d* configuration (Greenwood and Earnshaw, 1984). Reactions involving 1:3 and 1:2 metal to ligand ratio gave complexes which was formed from metal to ligand 1:3 and 1:2 stoichiometries respectively (Table 2). All the complexes were characterized with sharp melting points but poor solubility in organic solvents (Table 3).

Molar Conductance
Presented in Table 4 are the molar conductivities of the 1,10-phenanthroline complexes in water. These values indicate that they are the 1: 2 type electrolytes (Ahmed. *et al.,* 1966; Geary, 1971; Patel and Adeniyi, 1991).

Infrared spectra
The infrared spectra of the complexes (Figures l and 2; Table 5) were assigned by comparison with those of the ligands and related compounds. The interpretation of the spectra of 1,10-phenanthroline and 4, 4'- bipyridine, their metal complexes and similar compounds were based on the assignment and identification of C-H, C=N, C=C, C-N, SCH, SCC, OH as well as MN and MNM bending vibrations (Inskeep, 1962; Referraro *et al.*, 1968; Patel and Adeniyi, 1991).

The broadness and complexity of the bands in the region 3000-3700 cm^{-1} in the complexes are due to the OH stretching vibrations and are attributed to the uncoordinated water molecule (Takemoto and Hutchinson, 1972; Pologikh *et al*., 1975; Cotton and Wilkinson, 1976; Clark *et al.*, 1977).

Table 1: Analytical Data of 1,10-phenanthroline and 4,4'-bipyridine complexes of manganese(II) tetrafluoroborate

Compound	Molecular Formula	Molecular mass	M..P. (°C)	Mn	C	H	N
$Mn(phen)_3(BF_4)_2.5H_2O$	$Mn(C_{12}H_8N_2)_3(BF_4)_2.5H_2O$	696.54	137-138	8.08 (7.88)	20.1 (20.67)	1.42 (1.44)	1.42 (1.44)
$[Mn(bipy)(BF_4)_2]$	$Mn(C_{10}H_8N_2)_3(BF_4)_2$	384.728	237-238	13.98 (14.28)	31.21	2.1	7.3 (7.27)

Figures in parentheses are the calculated values

Table 2: Physical data on divalent complex of manganese tetrafluoroborate

Properties/Compound	$Mn(BF_4)_2.6H_2O$	$Mn(phen)_3(BF_4)_2.5H_2O$	$[Mn(bipy)(BF_4)_2]$
Proposed molecular formula		$Mn(C_{12}H_8N_2)_3(BF_4)_2.5H_2O$	$Mn(C_{10}H_8N_2)_3(BF_4)_2$
Molecular mass	336.64	696.54	384.728
MP/Decomp	Hygroscopic	137-138	237-238
Found (%)	16.32	8.08	13.98
Calculated (%)	15.43	7.88	14.03
Yield (%)	53	35	23

Table 3: Solubility of 1,10-phenanthroline and 4,4'-bipyridine complexes of manganese(II) in selected solvents.

	$Mn(phen)_3(BF_4)_2.5H_2O$	$Mn(bipy)(BF_4)_2$
Water	S	IS
Methanol	SS	IS
Ethanol	IS	IS
THF	IS	IS
Acetone	S	IS
1,4 Dioxane	IS	IS
DMSO	S	IS
N. Benzene	VSS	IS
Benzene	IS	IS
Ether	IS	IS

S=soluble; IS=Insoluble; SS=slightly soluble; VSS=very slightly soluble.

Table 4: Molar conductance of manganese(II) tetrafluoroborate and 1,10-phenanthroline complexes of Mn(II) tetrafluoroborate.

	$Mn(BF_4)_2.6H_2O$	$Mn(phen)_3(BF_4)_2.5H_2O$
Concentration	3.0	3.1
Solution (Vm/cm^3)	33333.33	322580.645
Electrolytic conductivity $K/scxm^{-1}$	0.0001603	0.000443
Molar conductance vm/scm^2mol	201	143
Probable electrolyte	2:1	2:1

Table 5: Infra red spectra data (cm^{-1}) of 1,10-Phenanthroline and 4,4'-bipyridine complexes of manganese(II)

Compound	?C-H	?C=N	?C=C	?CH	?C-N	BF_4 ligand mode
1,10-Phenanthroline	3060	2460	1620	1470	1390	-
$Mn(phen)_3(BF_4)_2$	3045	2375	1601	1461	1341	1100,521
4,4'-bipyridine		2420	1601	1465	1235	-
$Mn(bipy)(BF_4)_2$		2409	1535	1415	1226	1070

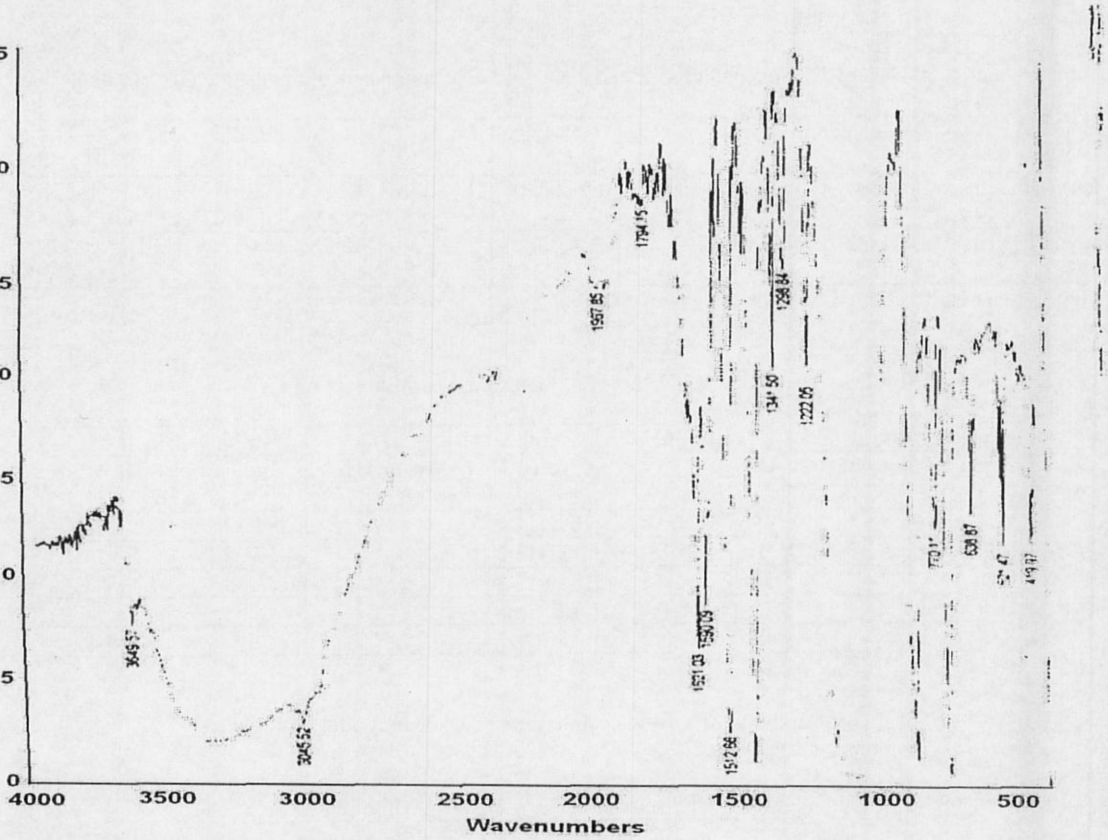

Fig. 1: Infrared spectrum of [Mn (phen)$_3$] (BF$^-_4$)$_2$.4H$_2$O

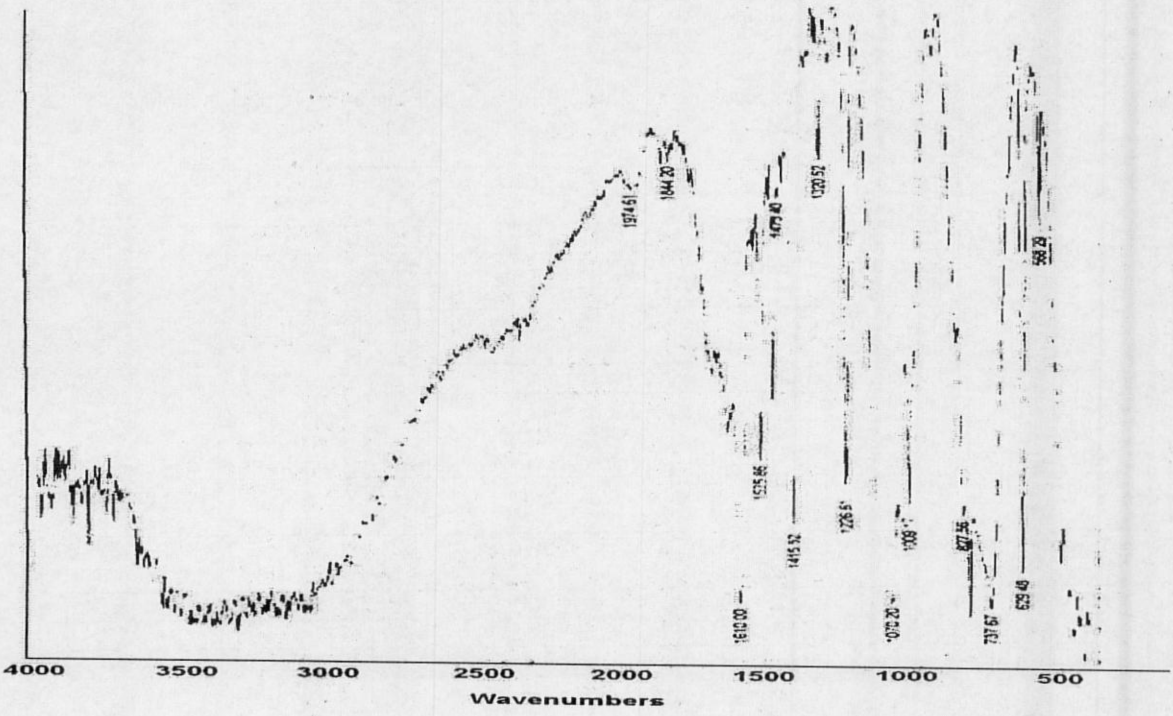

Fig. 2: Infrared spectrum of [Mn (bipy) (BF$^-_4$)$_2$]

The bands in the high frequency region of 1,10-Phenanthroline and in the bipyridine metal complexes are not metal sensitive since they originate in the heterocyclic or aromatic ring of the ligand (Takemoto and Hutchinson, 1972; Cotton and Wilkinson, 1976; Laptowski and Muecyslalw, 1980).

Hutchinson *et al.* (1970) observed that bands in the high frequency region are due to ligand vibrations slightly perturbed by coordination. The MN stretching and bending vibrations originate below 300 cm^{-1} and due to instrumental limitation could not be read. Since bond energy is lowered in bond formation, then when frequencies are lowered in the spectra compared to that of the ligand suggest bonding as increased frequency indicates non-coordination because vibration energy increases due to back donation of electrons by the metal ion to the ligand on coordination (Xiangym and Zhengzhong, 1985).

In 1,10-Phenanthroline complexes the band around 3060 cm^{-1} in the free ligand decreased on complexation to 3045 and 3058 cm^{-1}. Bands around 2460 cm^{-1} and in the ligand also decreased due to complexation to 2375, 2370, 2351 and 2351 cm^{-1} as well as the bands around 1390 cm^{-1} in the free ligand to 1341-1347 cm^{-1} in the metal complex.

The bands around 2830, 2070, 1180, 1160 cm^{-1} disappeared in the metal complexes due to bonding through other atoms other than nitrogen. The bands at 1130-1100 cm^{-1} are due to BF_4 stretching while those at 535-530 cm^{-1} are due to BF_4 deformation (Akimor *et al.*, 1970).

The absence of bands around 680-750 cm^{-1} suggests the absence of M-OH vibrations thus all the water molecules are in the outer sphere of the complex.

The spectrum of the pyridine metal complex is complicated due to the presence of impurities as its insolubility precluded recrystallization hence the purity could not be ascertained although there are evidences for the complex formation. For example the bands around 2420 and 1235 cm^{-1} in the free ligand decreased to 2409 and 1226 cm^{-1} in the complex. The bands around 3600-3500 cm^{-1} in the bipyridine complexes are attributable to the water molecule entrapped but not coordinated in the lattice of the complex, as 1630-1600 cm^{-1} bands are absent. Based on the analytical and physicochemical data of the complexes the presumed structures (I-IV) of these complexes are with no indication of BF_4^- anion coordination (Fig. 3). The absence of x-ray studies makes the structural deductions tentative.

4. Conclusion

The infrared spectra showed the coordination of the ligands to the metal ions. The coordination was through the nitrogen atoms of the ligand.

The molar conductance of the 1,10-Phenanthroline metal complexes in water indicated a 2:1 type electrolytes, which is an indication that the $[BF^-_4]$ anion is not, coordinated in the complex but in the outer sphere.

The 4,4'-bipyridine complexes are probably polymeric due to their insolubility and high thermal stability.

REFERENCES

Ahmed, A.D., Mandal, P.K. and Chaudri, N.R., 1966. Metal complexes of malonic dihydride. *Journ. Inorg and Nuclear Chemistry* 28, 2951-2959.

Akimor, S.T., Druzhinim, I.G. and Rydyver, M., 1970. Reactions of 2,2' bipyridyl and 1,10-Phenanthroline with transition metal salts. *IZV Akad kirg, USSR* 5, 36-37.

Basset, J., Cdenny, R., Jeffrey, G.H. and Mendham, J. (eds.), 1985. Vogel's Textbook of Qualitative Inorganic Analysis (4th ed.). ELBS/Longman. London.

Buckingham, H.J., 1982. Dictionary of Organic Compounds (5th edition). Chapman Newman Company (New York) pp. 2655-2656.

Clark, R.J.H., Turtle, P.C., Strommen, D.P., Streusand, B., Kincard, J. and Nakamoto, K. 1977. *Inorganic Chemistry* 1684-86.

Cole, H.I., 1973. 1,10-Phenanthroline as a reagent in qualitative analysis. *Philippine Journ. Sci.* 22, 631-637.

Cotton, F.A. and Wilkinson, G., 1976. Basic Inorganic Chemistry (International Edition). John Wiley, London, 280pp.

Crowell, W.R. and Kong, O., 1968. 1,10 phenanthroline as a reagent for microscopic test. *Microchem ver mikrochim Acta.* 33, 303-309.

Dillard C.R. and Goldberg, D.E., 1978. Chemistry, Reactions, Structure and Properties (2nd edition). Macmillan and Sons Ltd., New York, pp. 263-266.

Dimroth, O. and Frister, R., 1921. Catalytic synthesis of 4, 4'bipyridine. *Journal of American Chemical Society* 22, 2061-2064

Elder, J.A., 1969. Inhibitors in metals corrosion U.S 2, 478-755.

Fielden and Summers, L.A., 1974. Chemical constitution and activity of bipyridine herbicides. *Summers Journal of Organic Chemistry* 36, 4089-

Geary, W.J., 1971. *Coordination Chemistry Review* 7, 81.

Greenwood, N.N. and Earnshaw, A., 1984. Chemistry of the Elements. Pergamon Press, New York. 1401pp.

Hathenway, B.J., and Undenhill, A.E., 1962. The preparation and properties of some divalent transitional tetrafluoroborate methyl cyanide complexes *Journal Chemical Society*, 2444-2449.

Helmont, S., 1986. Hydrophobic and stacking interactions in metal ion complexes containing co-enzyme. *Inorganic Biochem.* 85, 57-62.

Horold and Warren, K., 1981. Copper (II) complexes of 2,2' bipyridine and 1,10-phenanthroline. *Inorganic and Nuclear Chemistry* 43, 3165.

Hutchinson, B., Takemoto, J. and Nakamoto, K., 1970. Metal isotopic effect on metal ligand vibrations of tris complexes of 2,2'byrypyridine and 1,10-phenanthroline. *Journ. Amer. Chem. Soc.*, 92, 3335-3336.

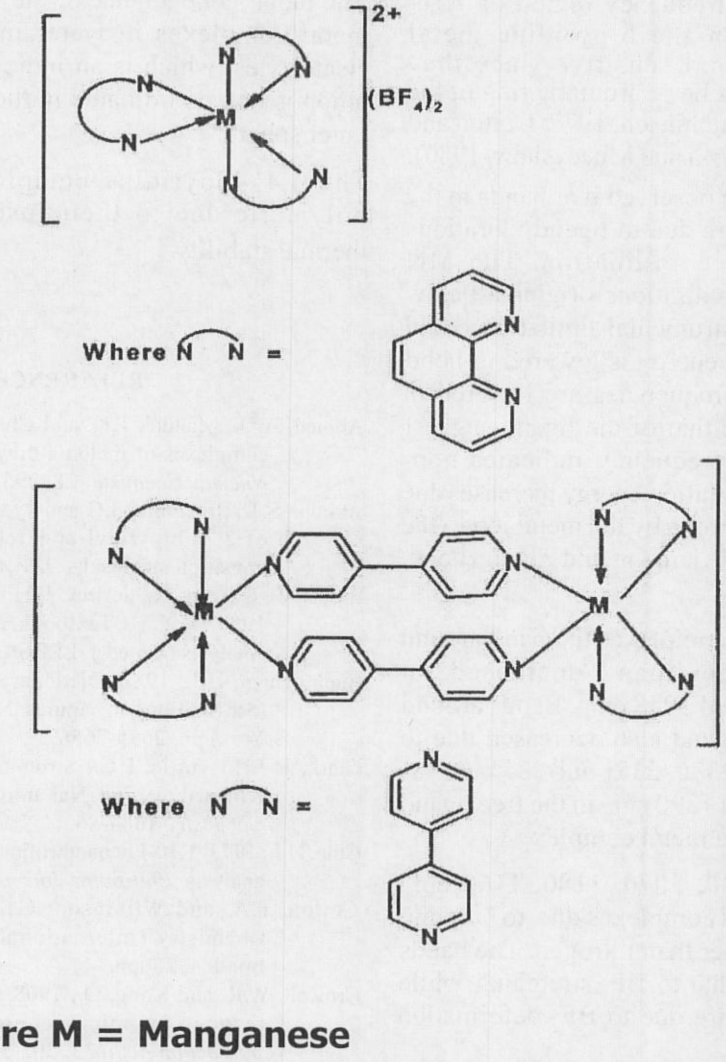

Fig. 3: Proposed structure for 1,10-phenanthroline and 4,4'-bipyridine complexes of manganese (II) tetrafluoroborate.

Inskeep, R.G., 1962. The spectra of the tris complexes of 1,10-phenthroline and 2,2'bipyridine with transition metals iron (II) through zinc (II). *Journal of Inorganic and Nuclear Chemistry* 24, 763-768.

Kalo, M., Jonassen, and Fanning, J.C., 1964. Complexes of Copper (II). *Coordination Chemistry Review* 64, 99-106.

Kazybaev, S.A., Yun, P.T., Ymananakkunor, B.I. and Bruzinn, I.G., 1972. Reactions of 1,10-phenanthroline with strontium and barium chloride. *Russian Journal of Inorganic Chemistry* 17, 1050-1051.

Laptowski, M. and Muecyslalw, S., 1980. Copper (II) complexes 2,2'bipyridine and 1,10-phenanthroline. *Russian Journal of Inorganic Chemistry* 25, 987-989.

Lever, A.B., Lewis, J. and Nylom, 1964. Polymeric nickel compounds with 4,4' bipyridine. *Journ. Chem. Soc.*54, 4 761-4762.

Musgrave, T.A. and Mattson, C.C., 1968. Coordination Chemistry of 4,4'bipyridine. *Inorganic Chemistry* 7, 1434-1436.

Nagasawa R., Michctaro, N., Norihiko, W., Watenebe, C. and Hironaga, F., 1970. 2,2' bipyridine in the degradation of cholesterol. *Agric Biol. Chem*. 34, 838-844.

Patel, K.S. and Adeniyi, A.A., 1991. Dicarboxylic Acid Hydrazide complexes of copper(II) Tetrafluoroborate. *Synthesis and reactivity in Inorganic Metal-Organic Chemistry* 21, 1351-1364.

Peard, W. and Flaun, R., 1958. Complexes of 4,4'-bipyridine with silver salts. *Journ. Amer. Chem. Soc.* 80, 1593-1596.

Pologikh, L.V., Kevach, P.I. and Statehova, A.H., 1975. Infrared spectra and structure of the complexes formed by hexamethylene tetramine with crystalline hydrated perchlorates of bivalent metals and $MgCl_2$. *Russian Journal of Inorganic Chemistry* 20, 1769-1773.

Pyanoski, N. and Sutzhanov, N.R., 1984. Protective coating and fast driers in paint and related products. *Journal of Bangladesh Acad. of Science* 7, 39-47.

Raa, V., Randu, S.R. and Bhaskara, V., 1970. Effect of inhibitors on the corrosion of iron. *Indian Journ. Chem.* 52, 285.

Scagliarini, G. and Cosari, G.C., 1964. Addition compounds between Halides and bivalent metal organic bases. *Grazz Chim Ital* 64, 742-745.

Sigel, H., 1986. Hydrophobic and stacking interactions in metal ion complexes containing coenzyme. *Inorganic Biochemistry* 85, 57-62.

Sleer, B.T. and Gibbs, 1969. 1,10 phenanthroline as fertilizer. *Molecular Physiol*. 44(5), 781-783.

Smith, C.R., 1924. Synthesis and properties of 4,4'bipyridine. *Journal Amer. Chem. Soc*. 46, 414-415.

Takemoto, J. and Hutchinson, B., 1972. Inorganic and Nuclear Chemical letters 8, 769.

Xiangym, Du and Zhengzhong, H., 1985. Catalytic paleographic determination of micro amount of cadmium. *Z Inorg. Allg Chem.* 37, 186.

Yavoski, N.P. and Sutzhanov, N.B., 1970. Complexes of cadmium thiocyanate and bromide with 2,2'bipyridine and 1,10 phenanthroline. *Russian Journal of Inorganic Chemistry* 13, 438-440.

Yean, D.C., 1983. Determination of hexacyanano ferrates in water. *Fektion Kranth* 129, 53-62.

Young, Maitland, C. and Wang, J., 1971. Coenzyme competitive inhibitors. *Journ. Biol. Chem*. 9, 2815.