ABSTRACT

A new series of Cr(III), Mn(II), Fe(II), Co(II) and Ni(II) complexes of the 3-hydrazino benzoxazine-2-one (HBO) were prepared and characterized. The ligand behaves as a bis bidentate ONNN donor. The nature of bonding and the stereochemistry of the complexes have been deduced from elemental analyses, thermal, infrared, electronic spectra, magnetic susceptibility and conductivity measurements. An octahedral geometry was suggested for all the complexes. All the complexes show subnormal magnetic moments. The ligand, HBO, and its complexes were tested against Neurospora crassa, a non-pathogenic fungus. The Mn(II) and Co(II) complexes exhibited higher antifungal activities than the parent ligand.

Keywords: Bis bidentate donor, Subnormal magnetic moments, Octahedral geometry Antifungal activity.

INTRODUCTION

Benzoxazines are an important class of oxygen-nitrogen heterocyclic compounds with a variety of biological activities, specifically as antimicrobial[1], antifungal[2,3], antiangiogenic therapeutic agents[4], antiarrhythmic[5], neuropeptide y5 antagonists[6], neuroprotective agents[7], estrogen receptorβ agonists[8], antimycobacterial agents[9]. Metal complexes of benzoxazine derivatives [10] have received less attention inspite of their potential metal binding properties and promising applicabilities. Importance was hence given to studying these systems in our laboratories. In view of the importance of such benzoxazines, we describe here the
synthesis and characterization of Cr(II), Mn(II), Fe(II), Co(II) and Ni(II) complexes of the 3-hydrazino benzoxazine-2-one (HBO).

**MATERIALS AND METHODS**

All the chemicals used were either of AR or chemically pure grade. Mass spectrum was recorded on a PerkinElmer Hitachi-RMU-61 spectrometer and 1H NMR spectrum was recorded in DMSO-d₆ at room temperature using TMS as internal standard on a Varian XL-200MHz. IR spectra were recorded using KBr discs in the 4000–400 cm⁻¹ region on a Schimadzu IR-435 and in Nujol media in the 1000–200 cm⁻¹ region on a PerkinElmer IR spectrometer Model No 7. Electronic spectra of solids were recorded on a Cary-2390 UV–Vis-NIR spectrophotometer. The elemental analysis was carried out using Heraus-CHN-rapid analyzer. Chloride analysis was carried out by Mohr’s method. Metal contents were estimated using Labtam Plasma Scan-8410. Magnetic susceptibilities of complexes were measured on a Faraday balance CAHN-7550-03 USA at room temperature using Hg[Co(NCS)₄] as calibrant. Diamagnetic correction using Pascal’s constants and temperature independent paramagnetic corrections were computed [11]. The electrical conductance measurements were recorded using 10⁻³ M solutions in DMSO with an Elico digital conductivity bridge (Model CM-180) and dip type cell calibrated with KCl solutions. DTA was carried out using a Lead and Northup-USA instrument and TGA on a PerkinElmer model TGS-2 instrument.

**Synthesis of the ligand:** The ligand was synthesized in two steps. The first step is the synthesis of 1,4 benzoxazine-2,3-dione by reported method [12], followed by the synthesis of the 3-hydrazino benzoxazine-2-one (HBO) in the second step. 1,4-benzoxazine-2,3-dione (1gm) was dissolved in methanol (30ml). To this 15ml of hydrazine hydrate was added. The reaction mixture was heated under reflux for two hours. The contents were cooled to room temperature. Light brown colored compound was separated which was filtered and washed several times with methanol, petroleum ether. The compound was recrystallised from water and dried in vacuum.

**Synthesis of metal complexes:** A general method was adopted for the preparation of all the complexes. An aqueous solution of the ligand (0.002 moles) was added in small increments to an aqueous solution of the metal chloride (0.001 moles). The pH of the reaction mixture was then raised to 7–8 using a 1% aqueous ammonia solution. The reaction mixture was refluxed for 4-5 h. The colored product obtained was filtered hot and washed several times with small increments of distilled water, acetone and petroleum ether. Finally the complexes were washed with petroleum ether and dried in vacuum desiccators over anhydrous CaCl₂.

**Pharmacology:** A wild stain of Neurospora crassa (FGSC # 42000), obtained from Fungalnetics Stock Centre, Kansas City, U.S.A., was grown and maintained on a basal medium containing (G/100 ml) glucose, 2; Ammonium nitrate, 0.2; ammonium nitrate, 0.1; KH₂BO₄, 0.03; NaCl, 0.01; CaCl₂, 0.01; MgSO₄ • 7H₂O, 0.05, trace elements included as sulphates were (mg/100 ml) zinc, 20; manganese 20; iron 10; copper 8; ammonium molybdate, 2; biotin was added to final concentration of 0.5 (µ/100 ml). The organism was maintained by weekly subcultures on 2% agar slants, sterilization of media was carried out by autoclaving at 15 Lb/inch for 15 minutes. The organism was grown in 10 ml basal medium for 48 hours at 30° C, pH 4.8-5.0 in 50 ml conical flasks.
The metal salts, ligand, metal complexes and related compounds were aseptically added in solid form to the medium. A thick conical suspension of Neurospora crassa prepared from 7-10 days agar slant was inoculated into the medium (2-3 drops/flash). Cultures were incubated at 30°C for 2-3 days. At the end of incubation period the mycelia were harvested by filtration washed with distilled water and dried at 60°C overnight in hot air oven. The dry weight of the mycelium was recorded as the growth parameter and the inhibition of the growth by each of these compounds was calculated as percentage inhibition against the control culture (without added compounds) as follows:

(a) Dry weight of mycelium in control system = X gms
(b) Dry weight of mycelium in non-control system at different concentration Y gms

% of growth inhibition by compound (IB) = (Y/X x 100) - 100

All the growth experiments were repeated at least three times and only the average values were used to express the results.

RESULTS AND DISCUSSION

**Characterization of the ligand:** The ligand was characterized by elemental analysis (Table 1), IR (Table 2), $^1$H NMR and mass spectral studies. The analytical data reveals that the molecular formula of HBO is $C_8H_9N_3O_3$. The data suggests the formation of HBO as a monohydrate resulting from 1:1 condensation of 1, 4-benzoxazine-2, 3-dione and hydrazine hydrate. HBO is very much soluble in water and has poor solubility in other polar and non-polar solvents.

<table>
<thead>
<tr>
<th>Complexes with molecular formula</th>
<th>Calcd. (Found) %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metal</td>
</tr>
<tr>
<td>HBO.H$_2$O ($C_8H_9N_3O_3$)</td>
<td>–</td>
</tr>
<tr>
<td>[Cr$_3$(HBO)$_2$(NH$_3$)$_4$Cl$_6$]</td>
<td>19.71</td>
</tr>
<tr>
<td>($Cr_3C_16H_26N_{10}O_{4}Cl_6$)</td>
<td>(19.00)</td>
</tr>
<tr>
<td>[Mn$_3$(HBO)$_2$H$_2$O(NH$_3$)$_3$Cl$_6$]</td>
<td>20.57</td>
</tr>
<tr>
<td>($Mn_3C_16H_25N_9O_5Cl_6$)</td>
<td>(20.50)</td>
</tr>
<tr>
<td>[Fe$_3$(HBO)$_2$H$_2$OCl$_6$]</td>
<td>20.77</td>
</tr>
<tr>
<td>($Fe_3C_16H_22N_6O_8Cl_6$)</td>
<td>(20.20)</td>
</tr>
<tr>
<td>[Co$_3$(HBO)$_2$(NH$_3$)$_4$Cl$_6$]</td>
<td>21.78</td>
</tr>
<tr>
<td>($Co_3C_16H_25N_{10}O_{4}Cl_6$)</td>
<td>(21.80)</td>
</tr>
<tr>
<td>[Ni$_3$(HBO)$_2$(NH$_3$)$_4$Cl$_6$]</td>
<td>21.71</td>
</tr>
<tr>
<td>($Cr_3C_16H_25N_{10}O_{4}Cl_6$)</td>
<td>(21.50)</td>
</tr>
</tbody>
</table>

$^1$H-NMR spectrum of HBO in DMSO-d$_6$ solution indicates the existence of two possible tautomeric forms (Fig.1). The spectrum does not show satisfactory resolution due to poor solubility of HBO in DMSO. The two protons of NH$_2$ (hydrazine moiety) are resonated at $\delta$ 4.23. The proton of NH is resonated at $\delta$ 7.8 which may be attributed to intramolecular hydrogen bonding. The broad signal which appeared at $\delta$ 9.75-9.26 can be attributed to the ring NH. Both the NH groups’ signals appear at lower field due to the involvement of the hydrogens of these groups in intramolecular hydrogen bonding in the respective tautomeric structures I & II. The
protons of benzene ring appear as multiplet at δ 6.33-7.00. The integral strengths and ratios of the proton agree with the expected structure.

\[
\text{Fig 1. Tautomeric forms of HBO}
\]

The IR spectrum of HBO exhibits two sharp bands at 3284 cm\(^{-1}\) and 3179 cm\(^{-1}\) which can be assigned to asymmetric and symmetric stretching vibrations corresponding to terminal \(\nu\)\(\text{NH}_2\) group of hydrazine. The lower frequency of these vibrations is due to hydrogen bonding. The peak observed in the region of 3011 cm\(^{-1}\) can be attributed to intramolecular hydrogen bonded –\(\text{NH}\) of hydrazine side chain. The spectrum presents a sharp band at 1680 cm\(^{-1}\) which is the characteristic of \(\nu\)\(\text{C}=\text{O}\) (lactone). The band appearing at 1610 cm\(^{-1}\) with a shoulder can be assigned to azomethine (ring) along with the deformation modes of \(\nu\text{NH}\), \(\nu\text{NH}_2\) in admixture.

The tautomerism of ring azomethine – HBO to exocyclic azomethine –HBO was restricted due to the intramolecular hydrogen bonding between –\(\text{NH}\) and lactone carbonyl oxygen, and also between \(\text{NH}_2\) and azomethine (ring) nitrogen. Because of this, it is assumed that \(\nu\)\(\text{C} = \text{N}\) (ring) appears at higher frequency than expected. The spectrum also presents a band at 1098 cm\(^{-1}\), which can be attributed to \(\nu\)\(\text{N} = \text{N}\) of hydrazine moiety. The IR spectral data supports the existence of HBO in solid state as in structure II in figure 1.

The electronic spectrum of HBO shows several absorption bands, which are consistent with the expected structure. The bands observed at 47619-42553 cm\(^{-1}\) can be assigned to the \(\pi-\pi^*\) transitions of benzene ring. The spectrum has shown bands at 38461 cm\(^{-1}\), 35714 cm\(^{-1}\), which can be assigned to the benzoazine function and hydrazine side chain. The band observed at 30303 cm\(^{-1}\) is pertaining to the electronic transition of lactone carbonyl group. The spectrum has also shown a band at 22222 cm\(^{-1}\) which can be attributed to ring azomethine.

**Characterization of complexes:** All the complexes are colored and stable in air. They are insoluble in common organic solvents but soluble in DMSO and DMF. They do not melt or decompose until 300\(^\circ\) C. The elemental analysis of metal complexes (Table 1) suggests metal to ligand ratio as 3:2. It also suggests metal to chloride ratio as 1:2. The data also suggests the presence of coordinated ammonia and water in the complexes. The conductance data show that all are non-electrolytes. This suggests that the chlorides in all the complexes are with in the coordination sphere. TGA/DTA studies show that Mn(II) and Fe(II) complexes show endotherms in the range of 180 – 245\(^\circ\) C corresponding to deaquation which is in agreement with the proposed formulae. Elimination of water takes place in a single step in Mn(II) complex, while the same is a two step process in Fe(II) complex at 220\(^\circ\) & 245\(^\circ\)C [13].

The infrared spectra of the metal complexes exhibit characteristic changes with the free ligand spectrum (Table 2). A negative shift in \(\nu\text{C}=\text{O}\) and \(\nu\text{C}=\text{N}\) (ring) support the involvement of
The ligand while employing the exocyclic lactone carbonyl and ring azomethine groups in coordination cannot stand for reasoning with respect to chelation. This is because these two groups are separated by a distance which in no way result in stable chelate formation. At the same time the conclusive evidence produced by the infrared spectra of metal complexes in support of the involvement of these two groups in coordination cannot be overlooked. Hence, it is assumed that the hydrazino moiety is also associated with metal binding process. From the analytical data it is suggested that ammonia molecules are also present in the complexes. They indicate their presence as very strong multiple bands in the region of 3166-3400 cm\(^{-1}\) in all the complexes except Fe(II) [16]. Due to the presence of these bands it is not possible to gather any conclusive evidence regarding the changes with respect to \(\nu_{\text{N-H}}\) stretching of hydrazine moiety. Similarly the deformation modes also do not indicate themselves distinctly in 1600 cm\(^{-1}\) region. But the region assigned for \(\nu_{\text{C=O}}\) in the complexes seems to contain the components of these modes in admixture. In comparison with the position of these modes in the free ligand, their presence in the spectra of the complexes in the region at or above 1625 cm\(^{-1}\) indicating positive shift may be taken as an evidence for the involvement of both the nitrogens of hydrazine moiety in coordination. This assumption gains support from the large downward shift in \(\nu_{\text{N-N}}\) band in all the complexes [17].

As such it is concluded that the ligand HBO presents an unusual mode of metal binding which projects it as an ONNN donor. However, the possible mode of binding cannot involve a single metal ion. This mode can be justified by the trinuclearity of the complexes as indicated by the formulations worked out on the basis of elemental analysis.

### Table 2. Characteristic Infra red frequencies of HBO and its complexes (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Ligand/Complex</th>
<th>(\nu_{\text{NH2}}) (asym)</th>
<th>(\nu_{\text{NH2}}) (sym)</th>
<th>(\nu_{\text{NH}})</th>
<th>(\nu_{\text{C=O}})</th>
<th>(\nu_{\text{C=N}}) (ring)</th>
<th>(\nu_{\text{N-N}})</th>
<th>New Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBO.H(_2)O</td>
<td>3284</td>
<td>3179</td>
<td>3011</td>
<td>1681</td>
<td>1610</td>
<td>1098</td>
<td>–</td>
</tr>
<tr>
<td>([\text{Cr3(HBO)}_{3}(\text{NH}_3)_2\text{Cl}_6])</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1670</td>
<td>1583(sh)</td>
<td>950</td>
<td>3400-3166, 1280, 800,610, 570, 530, 480, 440, 280</td>
</tr>
<tr>
<td>([\text{Mn3(HBO)}_2\text{H}_2\text{O(NH}_3)_3\text{Cl}_6])</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1611</td>
<td>1542(sh)</td>
<td>957</td>
<td>3413-3189, 1274, 808, 611, 280, 252</td>
</tr>
<tr>
<td>([\text{Fe3(HBO)}_2(\text{H}_2\text{O})_4\text{Cl}_6])</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1625</td>
<td>1594(sh)</td>
<td>950</td>
<td>3402-3138, 1277, 912, 580, 275</td>
</tr>
<tr>
<td>([\text{Co3(HBO)}_2(\text{NH}_3)_2\text{Cl}_6])</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1625</td>
<td>1553(sh)</td>
<td>965</td>
<td>3400-3200, 1309, 805, 265</td>
</tr>
<tr>
<td>([\text{Ni3(HBO)}_2(\text{NH}_3)_2\text{Cl}_6])</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1624</td>
<td>1578(sh)</td>
<td>960</td>
<td>3400-3260, 1287, 960, 602, 290, 245</td>
</tr>
</tbody>
</table>

Additional features of the IR spectra of the complexes are the new bands observed in the range of 1270-1309 cm\(^{-1}\) assignable to new symmetric bending modes of coordinated ammonia molecules[16]. In support these rocking modes of coordinated ammonia are observed in the region of 602-805 cm\(^{-1}\). In Fe(II) and Mn(II) complexes there are non ligand bands of medium intensity at 912cm\(^{-1}\) and 808cm\(^{-1}\) respectively assignable to rocking modes of coordinated water[18]. The \(\nu_{\text{O-H}}, \nu_{\text{N-H}}\) stretchings in these complexes appear together as broad multi-structured bands. In Mn(II) complex the broad band is resolved into three components appearing at 3413 cm\(^{-1}\), 3283 cm\(^{-1}\), 3189 cm\(^{-1}\). Some more new bands of weak to medium intensity located in the region of 400 – 600cm\(^{-1}\) are attributed to \(\nu_{\text{M-O}, \nu_{\text{M-N}}}[19]. \nu_{\text{M-Cl}}\) vibrational modes.
have been observed in the range of 252-300 cm$^{-1}$ [20] in all the complexes, which provide conclusive evidence for the presence of chlorides in coordination sphere.

Magnetic susceptibilities observed at room temperature show strikingly subnormal values. The observed and expected magnetic moments are given in Table 3. The data show that iron complex is diamagnetic and the others are paramagnetic. The trivalent iron salt employed in the synthesis with d$^5$ configuration is expected to give magnetic moment equivalent to five unpaired electrons in high spin configuration, while the same should show one unpaired electron in low spin configuration. Both the possibilities are ruled out as the iron complex has been observed to be diamagnetic. Hydrazines and substituted hydrazines are known to behave as reducing agents. The ligand, HBO is a substituted hydrazine system and it is likely that the trivalent iron is reduced to divalent state and the divalent iron has formed a low spin, diamagnetic complex. The diamagnetic property of Fe(II) complex is due to strong field interaction of ligand giving rise to t$_{2g}^6$ e$_g^0$ electronic configuration with no unpaired electrons. Due to symmetric configuration there will not be any distortion of octahedral geometry in this complex. It may be recalled that the metal ion and the ligand were taken in 1:2 mole ratio for the synthesis of complexes. Analytical data shows 3:2 metal, ligand mole ratio in the complexes. This means a part of the ligand is acting as a reducing agent while the remaining is involved in metal binding process. The same reduction process is operative with respect to Cr(III) giving rise to Cr(II) complex, which is again preferring low spin state. In low spin state Cr(II) complexes with d$^4$ configurations are expected to give moments equivalent to two unpaired electrons. The present complex shows magnetic moment which is lower than the value expected for two unpaired electrons.

The sub normality in magnetic moments has been ascribed to anti ferromagnetism which is due to the interaction between electronic spins on neighboring metal ions. It is generally accepted that mechanism of the exchange interaction involves the mutual pairing of electronic spins via some form of orbital overlap. Anti ferromagnetic exchange may be metal–metal interaction or super exchange.

Metal–metal interaction involves direct overlap of orbitals containing the unpaired electrons, which influences the magnetic behavior where as super exchange involves the interaction of electrons with opposite spins on the two interacting ions via an intermediate diamagnetic anion(s) which results ineffective pairing leading to a minimum number of unpaired spins in the ground state of the system. Both the mechanisms seem to be operative in the complexes of HBO. However detailed cryomagnetic studies are required to give more evidence in this regard. [21]

Electronic spectral data are given in Table 3. In comparison with the free ligand spectrum they show characteristic features, which can be attributed to electron density reorganisation and metal ligand bonding through specific metal binding centres. The spectra of all the complexes show several bands which may be explained by assuming different environments around each metal ion. The richness of electronic spectral bands in these complexes is also a supporting evidence for the trinuclearity of the complexes [22].

Low spin Cr (II) species will have $^3{T_{1g}}$ ground term, which is not seriously subjected to John Teller effect. Tanabe-Sugano diagrams for d$^4$ configuration suggest that the lowest spin allowed
transition will be $^3T_1g \rightarrow ^3E_g$ $^{277}$. The broad band observed in the range of 15384 – 17857 cm$^{-1}$ with multiple structures may be attributed to this transition due to three Cr(II) centres with octahedral geometry in variable environments.

### Table 3. Magnetic and Electronic Spectral Data of Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\mu_{\text{eff}}$ (BM) observed</th>
<th>$\mu_{\text{eff}}$ (BM) Expected</th>
<th>Electronic spectral bands (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr$_3$(HBO)$_2$(NH$_3$)$_4$Cl$_6$]</td>
<td>1.93</td>
<td>3.88</td>
<td>17857, 17397, 16666, 15384</td>
</tr>
<tr>
<td>[Mn$_3$(HBO)$_2$(H$_2$O)(NH$_3$)$_3$Cl$_6$]</td>
<td>4.15</td>
<td>5.92</td>
<td>32258, 30769, 28985, 27777, 25000, 21276, 19602, 17241, 16000, 15384, 14925, 12121</td>
</tr>
<tr>
<td>[Fe$_3$(HBO)$_2$(H$_2$O)$_4$Cl$_6$]</td>
<td>_</td>
<td>_</td>
<td>26315, 25000, 23255, 17543, 15625, 14925</td>
</tr>
<tr>
<td>[Co$_3$(HBO)$_2$(NH$_3$)$_4$Cl$_6$]</td>
<td>2.93</td>
<td>4.7-5.2</td>
<td>I. 6329, 6802, 8196, 9433, 10000, 10639 II. 11363, 13157, 15873 III.19607, 24390, 3564</td>
</tr>
<tr>
<td>[Ni$_3$(HBO)$_2$(NH$_3$)$_4$Cl$_6$]</td>
<td>1.83</td>
<td>2.9-3.4</td>
<td>36315, 17857, 16949, 16129, 15625, 11235, 10309, 10000, 8849, 7300, 7142</td>
</tr>
</tbody>
</table>

Low spin Fe (II) complex is expected to give two spin allowed absorption bands corresponding to $^1A_1 \rightarrow ^3T_1$ and $^1A_1 \rightarrow ^3T_2$ transitions. In view of the trinuclearity and variable octahedral environments around each Fe (II) as suggested by analytical, spectral and magnetic data, the bands observed in the region of 14925, 15625 and 17543 cm$^{-1}$ are assigned to the lower energy transitions i.e. $^1A_1 \rightarrow ^3T_1$ while the other bands in the region of 23255, 25000 and 26315 cm$^{-1}$ are due to the $^1A_1 \rightarrow ^3T_2$ transitions.

The electronic spectrum of manganese (II) complex exhibits several weak bands in the high energy region 27777-32258, 19602-25000 and low energy region 12121-17241 cm$^{-1}$. These bands can be attributed to doubly forbidden transitions involving $^6A_1$ ground state and several possible higher energy quartet states including, $^4T_{1g}$, $^4T_{2g}$, $^4A_{1g}$, $^4T_{2g}$ (D), $^4E_g$ (D), $^4T_{1g}$ (P), $^4A_{2g}$ (F), $^4T_{1g}$ (F), $^4T_{2g}$ (F).

Cobalt (II) high spin electronic spectrum closely matches with the octahedral geometry. The spectrum has been broadly divided into three regions. I. 6329, 6802, 8196, 9433, 10000, 10639 cm$^{-1}$ (several shoulders) III. 19607, 24390, 3564 (multiple structure)

They are assigned to $^4A_{1g}$ (F)$\rightarrow^4T_{2g}$, $^4A_{1g}$ (F)$\rightarrow^4A_{2g}$ and $^4A_{1g}$ (F)$\rightarrow^4T_{1g}$ (F) respectively.

The electronic spectrum of Ni(II) complex also exhibits several bands. The bands at 7141, 7300, 3846, 10000, 10309, 11235 cm$^{-1}$ are due to $^3A_{2g} \rightarrow ^3T_{2g}$ transition. The bands at 14925, 15625, 16129, 16949 and 17857 cm$^{-1}$ are because of $^3A_{2g} \rightarrow ^3T_{2g}$ (F) transitions and the band around 26315 cm$^{-1}$ is due to $^3A_{2g} \rightarrow ^3T_{2g}$ (P) transitions in octahedral geometry.

**Anti-fungal activity:** The free ligand exhibited 66.7%, growth inhibition which is totally lost in iron complex. But the percentage inhibition attained by manganese and cobalt complexes is nearly 100%.
CONCLUSION

Based on the analytical, thermal, conductivity, infrared spectra, magnetic and electronic spectral data, trinuclear octahedral structures have been proposed for all the complexes. The structures are given in figure 2.

\[ M = \text{Cr(II), Co(II), Ni(II)} \quad X = Y = Z = \text{NH}_3 \]
\[ M = \text{Mn(II)} \quad X = Y = \text{NH}_3, \quad Z = \text{H}_2\text{O} \]
\[ M = \text{Fe(II)} \quad X = Y = Z = \text{H}_2\text{O} \]

Fig 2. Proposed structure of metal complexes

REFERENCES