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Synthesis and Characterization of 3D Transition Metal Complexes Derived from 2,3-bis(2-(2-nitrobenzylidene)hydrazinyl)quinoxaline.

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ABSTRACT

VO(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of 2,3-bis(2-(2-nitrobenzylidene)hydrazinyl)quinoxaline (BNBHQ) have been synthesized and characterized by elemental analysis, conductance, thermal, spectral and magnetic data. Octahedral geometries have been proposed for all the complexes. BNBHQ acts as a neutral bis-bidentate NN donor and is forming polynuclear complexes.

Keywords: BNBHQ, polynuclear, spectral, octahedral.

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INTRODUCTION

Quinoxalines are an important class of nitrogen-containing heterocycles with a variety of biological activities, specifically as AMPA/GlyN receptor antagonists [1-3], angiotensin II receptor antagonists [4,5], anticancer agents [6], anti-infection agents [7] and immune modulating agents [8]. Metal complexes of quinoxaline derivatives have received attention because of their potential metal binding properties and promising applicabilities [9-19].

EXPERIMENTAL

Materials and Method

All the chemicals used were either of AR or chemically pure grade. IR spectra were recorded using KBr discs in the 4000-400 cm^{-1} region on Perkin-Elmer 1600 series FT-IR and in Nujol media in the 1000-200 cm^{-1} region on a Perkin-Elmer IR spectrometer model NO.17. Electronic spectra of solids were recorded on a Cary-2390 UV-Vis-NIR spectrophotometer. The elemental analysis was carried out using Heraeus-CHN-rapid analyzer. The $^1\text{H-NMR}$ spectrum was recorded on XL-200 MHz spectrometer in DMSO- d_6 solvent. Metal contents were estimated using an AAS Perkin Elmer-2380. Magnetic susceptibilities of complexes were measured on a Faraday balance CAHN-7550-03 USA at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant. Diamagnetic corrections using Pascal's constants and temperature independent paramagnetic corrections were computed[20]. The electrical conductance measurements were recorded using 10^{-3} molar solutions in DMSO with an Elico conductivity bridge (Model CM-180) and dip type cell calibrated with KCl solutions. EPR was recorded on Jeol SE-3X spectrometer at RT and liquid nitrogen temperature.

Preparation of Ligand (BNBHQ)

BNBHQ was prepared by a four step process involving the synthesis of quinoxaline-2,3-dione[21], 2,3-dichloro quinoxaline [22] and 2,3-dihydrazino quinoxaline[11]. 2-nitro benzaldehyde (0.6 g) was added to a solution of 2,3-dihydrazino quinoxaline (0.36 g) in DMF (50 ml)/ The mixture was refluxed for 3 h and then it was poured into water. The brown colored compound that separated out was filtered and washed with small amounts of aqueous methanol. Then it was dried in *vacuo* and recrystallised from aqueous methanol Yield: 60%, m.p. 220 $^{\circ}\text{C}$ (Figure 1). Anal. found: C 58.76; H 3.50; N 24.35; calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_8\text{O}_4$: C 58.89; H 3.51; N 24.56 %. $[\text{M}^+]$ m/z 456. $^1\text{H NMR}$ (DMSO- d_6) δ : 7.3 – 8.0. (aromatic) (12), 8.5 (=CH-) (2) and 9,1 (-NH-) (2). IR bands (cm^{-1}): 3389 (νNH), 1631 ($\nu\text{C}=\text{N}$ free), 1600 ($\nu\text{C}=\text{N}$ ring), 1527 (νNO_2 asym), 1346 (νNO_2 sym) and 1025 ($\nu\text{N-N}$). UV-Vis (cm^{-1}): 43478 (benzene moiety), 37735 (NO_2), 24875, 23255 (free and ring azomethine).

Preparation of Metal Complexes

To a methanolic solution of divalent/trivalent metal chloride (0.001 mole) [Cr(III) (0.235 g); Mn(II) (0.19 g); Fe(III) (0.163 g); Co(II) (0.238 g); Ni(II) (0.237 g); Cu(II) (0.170 g) and Zn(II) (0.132 g)], methanolic solution of BNBHQ (0.001 mol, 0.3 g) was added. The pH of

the reaction mixture was adjusted to ~ 7 , using 5% methanolic ammonia solution. The mixture was refluxed for 3h. The complex which precipitated was filtered in hot condition, washed with methanol, petroleum-ether and dried *in vacuo*. In case of VO(II) complex vanadyl sulphate (0.162 g) was used and the same procedure was adopted. The purity of metal complexes was tested by TLC using different solvent mixtures. Yields: 50-70%.

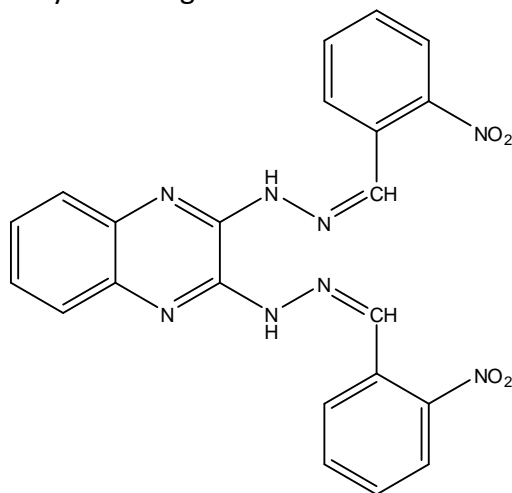


FIGURE 1: The ligand 2,3-bis(2-(2-nitrobenzylidene)hydrazinyl)quinoxaline (BNBHQ)

RESULTS AND DISCUSSION

The possible geometry of the Schiff base was evaluated using molecular calculation with arguslab software. The molecule was built and geometry optimization (Figure 2) was done using quantum mechanics (RHF) method. The Self consistent field (SCF) energy value is -122515.4112 kcal/mol.

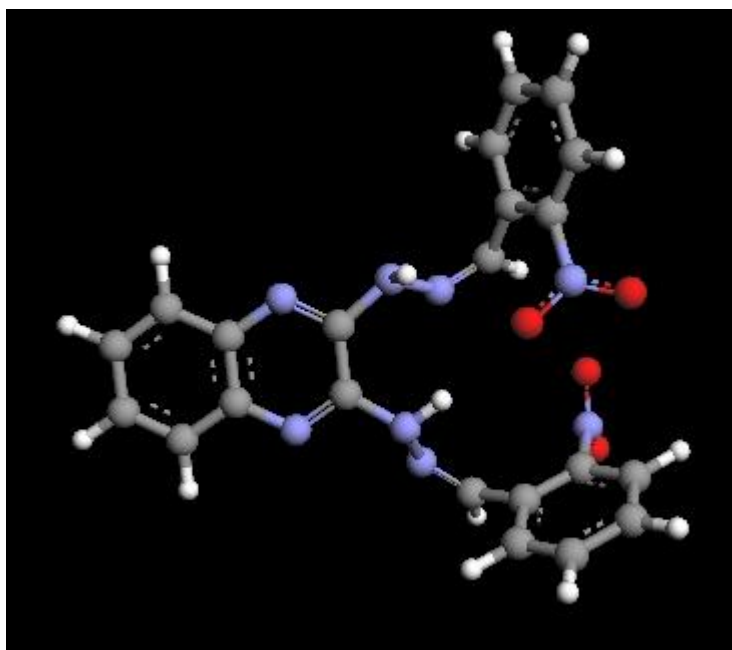


FIGURE 2: Geometry optimized structure of BNBHQ

Table 1: Analytical Data of Metal Complexes of BNBHQ

Compound	Experimental (Calcd.) %				
	M	C	H	N	S/ Cl
BNBHQ (C ₂₂ H ₁₆ N ₈ O ₄)	–	58.76(58.89)	3.50 (3.51)	24.35 (24.56)	–
[VOLSO ₄].3NH ₃	7.55 (7.61)	39.35 (39.40)	3.47 (3.43)	22.91 (21.27)	4.10 (4.15)
[Cr ₂ L(OH) ₄ Cl ₂ (NH ₃) ₂].4H ₂ O	12.59 (12.91)	32.70 (32.79)	4.24 (4.22)	17.29 (17.39)	8.79 (8.81)
[Mn ₂ L(OH) ₂ Cl ₂ (H ₂ O) ₂ (NH ₃) ₂].2H ₂ O	13.98 (14.16)	33.88 (33.98)	4.09 (4.11)	17.92 (18.02)	9.23 (9.20)
[Fe ₂ L(OH) ₄ Cl ₂ (H ₂ O) ₂].2H ₂ O	15.20 (15.07)	35.42 (35.53)	3.32 (3.23)	14.98 (15.07)	9.50 (9.55)
[Co ₂ L(OH) ₂ Cl ₂ (H ₂ O) ₂ (NH ₃) ₂]	15.16 (15.01)	33.61 (33.58)	3.34 (3.30)	17.99 (17.81)	9.08 (9.03)
[NiL(OH)Cl].2NH ₃	9.48 (9.65)	44.11 (43.92)	3.74 (3.82)	23.36 (23.29)	5.50 (5.58)
[CuL(OH)Cl]	11.78 (11.10)	46.23 (46.15)	2.99 (2.97)	19.54 (19.58)	5.97 (6.21)
[Zn ₃ LCl ₆ (H ₂ O) ₂]	21.66 (21.74)	29.40 (29.30)	2.29 (2.22)	12.44 (12.43)	23.60 (23.64)

All the metal complexes are coloured and stable to air and moisture. They decompose at high temperatures. They are soluble in DMF and DMSO and insoluble in all other common organic solvents like methanol, chloroform, acetone etc. The analytical data of all the complexes are given in Table 1. The analytical data reveals a metal to ligand ratio of 1: 1 in VO(II), Ni(II), Cu(II) complexes, a ratio of 2: 1 in Cr (III), Mn(II), Fe(III), Co(II) complexes, and 3:1 in Zn(II) complex. The presence of one chloride per metal ion is indicated in all the complexes except in that of Zn(II) wherein two chlorides per metal ion have been indicated. The presence of two hydroxide ions per metal in Cr(III), Fe(III) and one hydroxide ion per metal in Mn(II), Co(II), Ni(II) and Cu(II) is also evidenced by analytical data. The data provides evidence for sulphate in VO(II) complex. In VO(II), Cr(III), Mn(II), Fe(III), Co(II) and Ni(II) complexes, the nitrogen and hydrogen contents suggest the presence of ammonia molecules in addition to the expected ligand and water molecules. The conductance studies were carried out in 1×10^{-3} M DMF solutions. The low molar conductance values of all the complexes indicate their non-electrolytic nature [23]. TG and DT analysis show that the Cr(III) and Mn (II) complexes have four and two moles of crystal water per mole of complex respectively as indicated by endotherms in the temperature range of 100-120°C. The loss of water occurs in a single step. In Mn(II), Fe(III), Co(II) and Zn(II) complexes, the endotherms in the temperature region 150-170°C can be attributed to one coordinated water molecule with each metal ion [24].

The IR spectral data of the complexes are given in Table 2. In all the complexes the broad and strong bands which appeared in the region $1616-1590\text{cm}^{-1}$ are attributed to $\nu\text{C}=\text{N}$ (exo) [25] as well as $\nu\text{C}=\text{N}$ (ring), when compared to The characteristic doublet with band structures at 1631cm^{-1} ($\nu\text{C}=\text{N}$ (exo)) and 1600cm^{-1} . ($\nu\text{C}=\text{N}$ (ring)), the corresponding band positions indicate negative shift suggesting that both azomethine nitrogens (ring as well as side chain) are participating in coordination through an NN sequence. The positive shift of $\nu\text{N}-\text{N}$ band by $23-61\text{cm}^{-1}$ in the spectra of complexes is further supporting the involvement of the azomethine nitrogen (belonging to the hydrazine side chain of the

ligand) in coordination. The asymmetric and symmetric stretching frequencies of $-\text{NO}_2$ group are unaltered during complexation thus indicating non-involvement of $-\text{NO}_2$ group in coordination[15]. In IR spectra of all the complexes the broad bands in the region $3450-3220\text{cm}^{-1}$ are assignable to a combination of νNH and νOH . The presence of hydroxyl ions in coordination is further supported by non-ligand bands in range $1149-1011\text{cm}^{-1}$ which due to M-OH bending modes[26]. Hence it is concluded that the ligand is employing four nitrogens (two from ring azomethines and two from exocyclic azomethines) in a bis-bidentate fashion. In Cr(III), Mn(II) and Co(II) complexes the non-ligand bands observed at 1301 and $650-619\text{cm}^{-1}$ are corresponding to symmetric bending and rocking modes of coordinated ammonia molecules[17]. These non-ligand bands are absent in the spectra of VO(II), Ni (II) complexes, indicating that the ammonia molecules in these are outside the coordination sphere. A strong non-ligand band in the VO(II) complex observed at 1097cm^{-1} is assigned to monodentate sulphate. A band at 973cm^{-1} is due to $\nu\text{V}=\text{O}$ stretching frequency[18]. In Mn(II), Fe(III) and Co(II) complexes the non-ligand bands at 815 , 849 and 938cm^{-1} are attributed to the rocking mode of coordinated water molecules. In Cr(III), Mn(II) and Zn(II) complexes, the broad troughs in the region $3450-3000\text{cm}^{-1}$ are indicative of νOH due to crystal water. The presence of coordinated and crystal water in the complexes is confirmed by TGA/DTA data. New bands in the far-IR region are attributed to the $\nu\text{M-O}$, $\nu\text{M-N}$ and $\nu\text{M-Cl}$ vibrations.

IR spectra of BNBHQ complexes.

Table 2: Characteristic Infra-red frequencies of BNBHQ and its complexes (cm^{-1})

Compound	$\nu(\text{NH}+\text{OH})$	$\nu(\text{C}=\text{N})$ free	$\nu(\text{C}=\text{N})$ ring	$\nu(\text{NO}_2)$ asym	$\nu(\text{NO}_2)$ sym	$\nu(\text{N}-\text{N})$	New Bands
BNBHQ	3389	1631	1600	1527	1346	1025	
$[\text{V}(\text{SO}_4)_4 \cdot 3\text{NH}_3]$	3550-3100	1418		1525	1345	1060	973,614,503
$[\text{Cr}_2\text{L}(\text{OH})_4\text{Cl}_2(\text{NH}_3)_2] \cdot 4\text{H}_2\text{O}$	3500-3000	1613		1530	1350	1053	650,524,450,300
$[\text{Mn}_2\text{L}(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2] \cdot 2\text{H}_2\text{O}$	3550-3100	1616		1530	1353	1086	1301,815,619,510,310
$[\text{Fe}_2\text{L}(\text{OH})_4\text{Cl}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	3500-3000	1607		1526	1346	1051	914,608,473,324
$[\text{Co}_2\text{L}(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_2(\text{NH}_3)_2]$	3500-3000	1600		1531	1349	1051	938,632,526,305
$[\text{NiL}(\text{OH})\text{Cl}] \cdot 2\text{NH}_3$	3450-3050	1590		1531	1345	1064	638,498,321
$[\text{CuL}(\text{OH})\text{Cl}]$	3500-3100	1616		1529	1343	1064	608,485,312
$[\text{Zn}_3\text{LCl}_6(\text{H}_2\text{O})_2]$	3550-3100	1602		1529	1350	1080	855,667,479,307

Magnetic data of BNBHQ metal complexes.

The VO(II) complex shows magnetic moment value of 1.9B.M., which is an expected value for a d^1 system. The magnetic moment of Cr(III) complex is 3.8 BM, which is consistent with the d^3 system. The magnetic moments of Mn(II) and Fe(III) complexes are 5.9 and 5.7 BM respectively. The magnetic moments of Co(II), Ni(II) and Cu(II) complexes

are 3.8, 3.35 and 2.0 BM respectively, which are in agreement with the presence of three, two and one unpaired electrons of d^7 , d^8 and d^9 systems respectively.

Electronic spectra of BNBHQ complexes

The electronic spectrum of VO(II) complex [27]. show three bands at 24213, 20790 and 18348 cm^{-1} which are assignable to ${}^2B_2 \rightarrow {}^2A_1$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2E$ transitions respectively of octahedral geometry¹. The electronic spectrum of Cr(III) complex shows the absorptions at 29761, 26178 and 21052 cm^{-1} , which are due to ${}^4A_2 \rightarrow {}^4T_2$, ${}^4A_2 \rightarrow {}^4T_1$ and ${}^4A_2 \rightarrow {}^4T_1(P)$ transitions respectively of octahedral geometry. The electronic spectrum of Mn(II) complex exhibits several weak absorptions at 31545, 28755, 22573, 16445. These are due to doubly forbidden d-d transitions. The electronic spectrum of Fe(III) complex exhibits a weak absorptions at 36900, 28248, 23923, 22471, 17761, 15948 cm^{-1} and cannot be assigned to specific transitions. Based on analysis, ir and magnetic data octahedral geometry has been proposed for Mn(II) and Fe(III) complexes. The electronic spectrum of Co(II) complex exhibits a multistructured band with two components in the region 22675-15723 cm^{-1} , which are assigned to ${}^4T_1 \rightarrow {}^4T_1(P)$ and ${}^4T_1 \rightarrow {}^4A_2$ transitions respectively. The electronic spectrum of Ni(II) complex exhibits the bands at 36764, 28571, 18975 and 13586 cm^{-1} . The band at 13586 cm^{-1} is assigned to spin-forbidden ${}^3A_2 \rightarrow {}^1E$ transition. The other bands are assigned to ${}^3A_2 \rightarrow {}^3T_1(P)$, ${}^3A_2 \rightarrow {}^3T_1$ and ${}^3A_2 \rightarrow {}^3T_2$ respectively. The B and β values for Ni(II) complex are 669 and 0.645 respectively. The electronic spectrum of Cu(II) complex exhibits the bands at 21186, 17761 and 15290 cm^{-1} which are assigned to ${}^2B_1 \rightarrow {}^2E$, ${}^2B_1 \rightarrow {}^2B_2$ and ${}^2B_1 \rightarrow {}^2A_1$ transitions respectively. The band at 28248 cm^{-1} is assigned to charge transfer. Based on these observations octahedral geometries for Co(II), Ni(II) complexes and distorted octahedral geometry for Cu(II) complex have been proposed.

ESR spectra of VO(II) and Cu(II) complexes

The ESR spectrum of VO(II) complex [28] recorded at room temperature is shown in Figure 3. The 'g' value evaluated for this spectrum is 2.0371 which is higher than the normally observed 'g' value for VO(II). The average value of hyperfine coupling constant (A) comes out to be 67.7G. These features of the ESR spectrum suggest that vanadyl ions involve themselves in strong exchange interactions. However, the appearance of weakly resolved hyperfine structure indicates that the unpaired electron in VO(II) is slightly less delocalized.

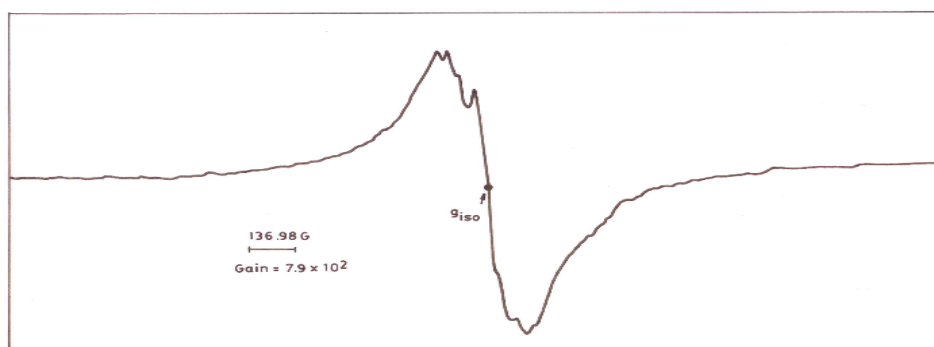


FIGURE 3: ESR spectrum of VO(II) complex

The ESR spectrum of Cu(II) complex recorded at room temperature for the powder sample is shown in Figure 4. The 'g' value evaluated for the intense signal comes out to be 2.0989, not far away from free electron 'g' value. The spectrum consists of almost a single signal and the 'g' value can be considered to be isotropic. This g_{iso} behaviour of Cu(II) complex justifies the conclusion that the complex consists of molecules in polymeric chains. The lack of well resolved hyperfine structure could be due to the exchange interactions in the Cu(II) paramagnetic ions.

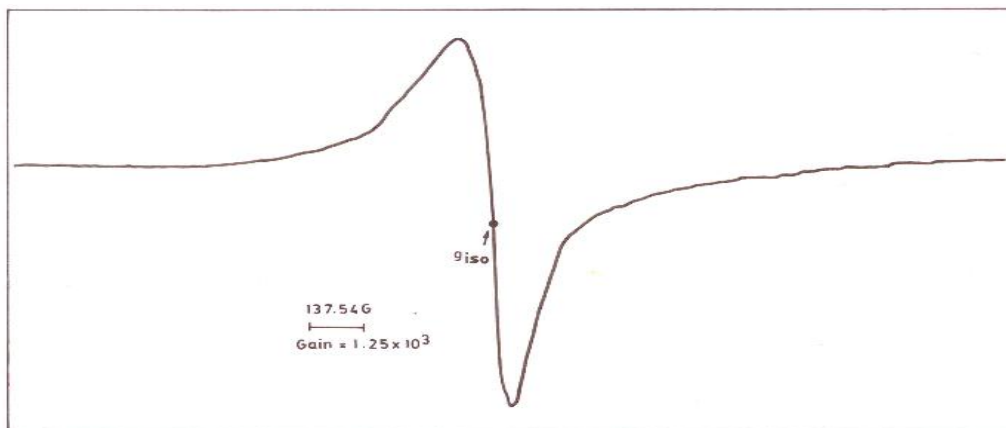


FIGURE 4: ESR spectrum of Cu(II) complex

CONCLUSION

Based on the analytical, spectral, thermal and magnetic data, it is proposed that BNBHQ is behaving as neutral bis-bidentate and is forming homo, bi and polynuclear complexes. However, the calculated magnetic moments don't show any subnormality for the simple reason that the metal ions in these complexes are well screened by the diamagnetic bulk of the large ligand molecules.

The proposed structures are given in Figures 5a – 5h.

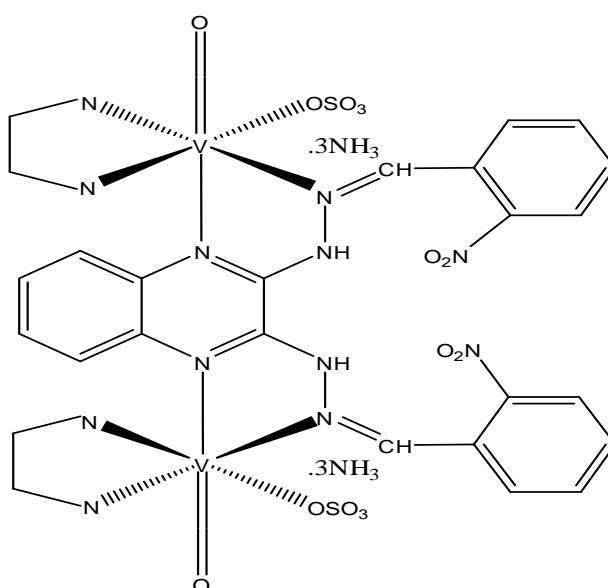


FIGURE 5a: Proposed structure of VO(II) complex

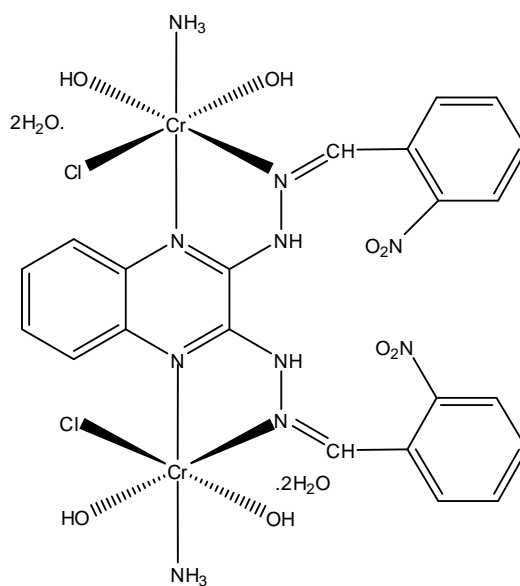


FIGURE 5b: Proposed structure of Cr(III) complex

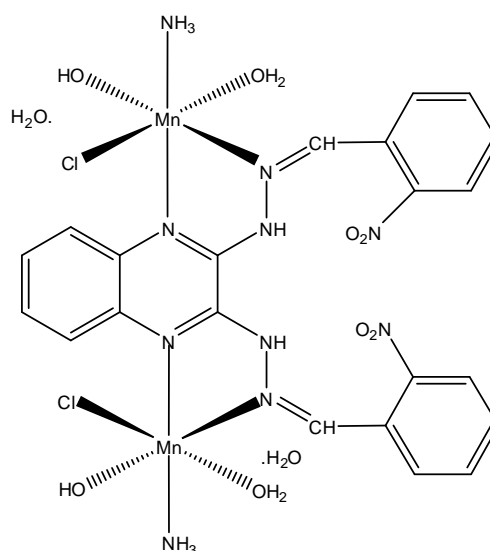


FIGURE 5c: Proposed structure of Mn(II) complex

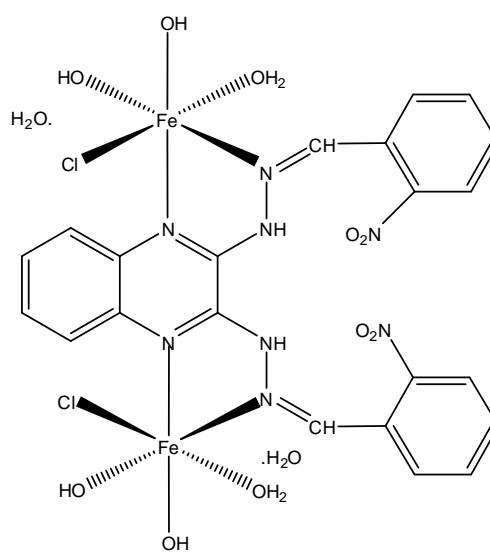


FIGURE 5d: Proposed structure of Fe(III) complex

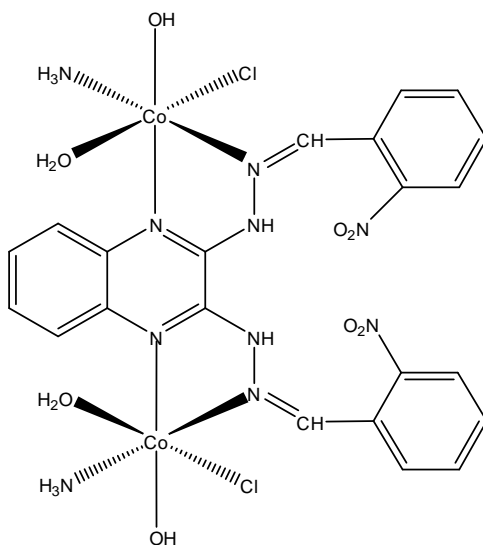


FIGURE 5e: Proposed structure of Co(II) complex

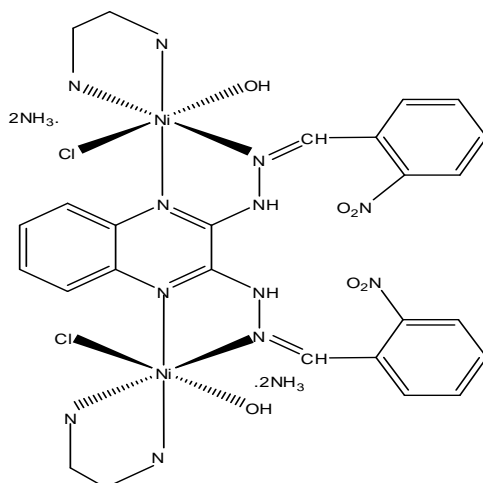


FIGURE 5f: Proposed structure of Ni(II) complex

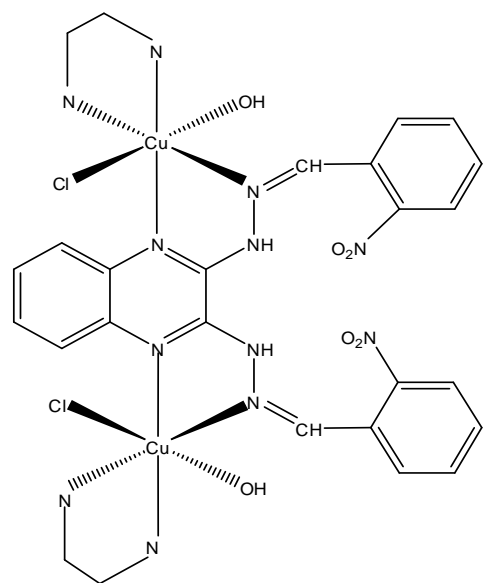


FIGURE 5g: Proposed structure of Cu(II) complex

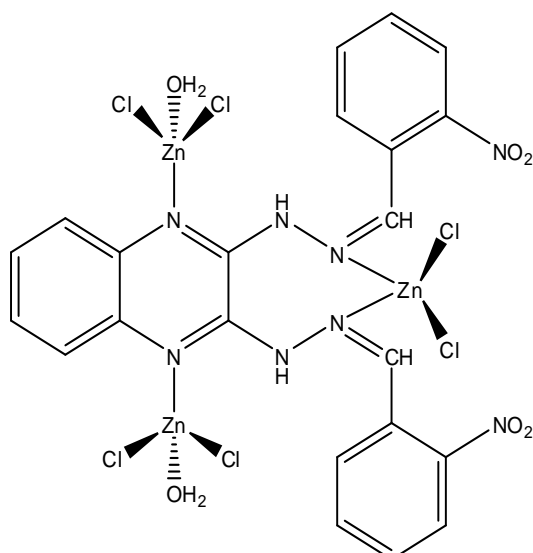


FIGURE 5h: Proposed structure of Zn(II) complex

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