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Synthesis and Characterization of 1-benzylbenzimidazole complexes with some transition metal salts

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ABSTRACT

New complexes of VO^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2} and Ag^{+} with 1-benzylbenzimidazole (Bbz) were synthesized by reaction of the ligand with suitable metal sources. The resulted complexes were isolated as a solid form with different colors and yield percentages. All the compounds were characterized by Uv-vis, FT-IR and CHN analysis techniques. Furthermore, ^{1}H NMR was used in characterization of the ligand only. According to the data resulted from the mentioned instrumental techniques, the structures for the prepared complexes were proposed as follows; square pyramid for VO^{+2}, tetrahedral for Co(II), square planar for Ni(II) and Cu(II), and linear for Ag(I).

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INTRODUCTION

Benzimidazole is aheterocyclic aromatic organic compound. This bicyclic compound consists of the fusion of benzene and imidazole. The most prominent benzimidazole compound in nature is N-ribosyl-dimethylbenzimidazole, which serves as an axial ligand for cobalt in vitamin B_{12}. Both Benzimidazole and imidazole act as good ligands to transition metal ions (Sundberg *et al*., 1974), and they exhibit different coordination modes as shown in Chart 1. Benzimidazole and imidazole ligands were used in the synthesis of different model complexes of metallo-enzymes such as hemocyanin, superoxide dismutase, and plastocyanin for copper and haemerythrin, methane monooxygenase, and ribonucleotide reductase for iron (Adams *et al*., 1990; Crane and Fenton, 1990).

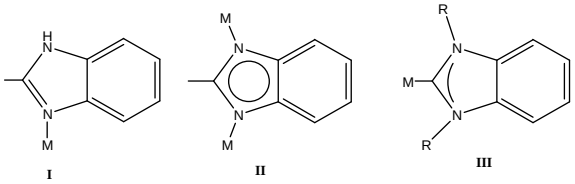

Chart 1: Coordination modes in benzimidazole.

Most of azoles including benzimidazole, in an extension of the well-elaborated imidazole system, have been used as carbon skeletons for N-heterocyclic carbenes (NHC), that are usually used as ligands for transition metal complexes. Benzimidazoles are involved in a great variety of biological processes. Some of their polyfunctional derivatives have been proved to possess antibacterial, fungicide and antihelmintic activity (Fabiola *et al*., 2008; Pawar *et al*., 2004; Mothilal *et al*., 2004; Özden *et al*., 2005). Therefore, substituted benzimidazoles have attracted the interest of various research groups. This interest was increased since it has been reported that the influence of the substitution at the 1, 2 and 5 positions of the benzimidazole ring is very important for their pharmacological effects (Ayhan-Kilcigil and Altanlar, 2006). Nevertheless, the biological studies of coordination compounds containing benzimidazole derivatives have been limited. Tavman and co-workers reported the synthesis of 4-Methoxy-2-(5-H/methyl/chloro/nitro-1H-benzimida-zol-2-yl)-phenol (HLX ; X=1-4) ligands and their complexes with $Fe(NO_3)_3$, $Cu(NO_3)_2$, $AgNO_3$, and $Zn(NO_3)_2$. The prepared complexes were evaluated against 9 types of bacteria and showed different activity (Tavman *et al*, 2009). Bajju and co-workers reported the synthesis and biological studies of porphyrinylChromium(III) benzimidazole complexes (Bajju *et al*., 2015). The prepared complexes showed negligible antibacterial and antioxidant behavior but well positive antifungal activity. In this study, the

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synthesis and characterization of some 1-benzylbenzimidazole coordination complexes with VO^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, and Ag^{+} are reported. In the prepared complexes, bonding occurs through the nitrogen atom in a monodentate form, regardless of the metal ion.

Experimental:

Material and measurements:

All the chemicals and solvent used were of reagent grade and used as it is without further purification. The FT-IR spectra of the compounds were recorded using an SHIMADZU spectrometer in the range 4000-400 cm^{-1}. NMR spectrum was recorded on Bruker 400 MHz Ultrashield^{TM} spectrometers at ambient temperature. ^{1}H peaks are labelled as singlet (s), doublet (d), triplet (t), and multiplet (m). Solvent signals were used as reference for the chemical shifts. The Uv-visible spectra were recorded using Sp-3000 nano OPTIMA spectrophotometer in range 200-800 nm. Elemental analysis CHN was carried by Euro element analysis CHNS, EA3000 analyzer.

Synthesis of the ligand 1-benzylbenzimidazole (Bbz):

In 250 ml round bottom flask containing 40 ml of DMSO, 2 g of NaOH and 5 g of benzimidazole was added. The mixture was heated using oil bath at 80-90 ^{o}C for 2 hr with constant stirring. The reaction mixture was slowly cooled to 40-50 ^{o}C, and benzyl bromide (7.5 ml) was added. The reaction was continued at the same condition for 1 hr. Then the mixture was poured in a 500 ml beaker immersed in ice-bath and containing 250 ml of distilled water. The resulted off-white precipitate left standing for 15 min, then collected by filtration and washed three times with cold distilled water then left to dry at room temperature. The yield percentage was 87.3 %. FT-IR cm^{-1} : 3440-3385 ν ($C_{ali\text{-}N\text{-}benz}$), 3130 and 3075 ν (C-H_{ar}), 2850-2900 ν (C-H_{aliph}), 1560–1590 ν (C=N), 800-640 δ (C-H_{ar}) . ^{1}H NMR (400 MHz, DMSO-d^{6}) δppm: 5.49 (s, 2H, benzylic CH_2), 7.17-7.44 (m, 5H, Ar_{bz}-H), 7.5 (t, 2H, Ar_{bzim}-H), 7.64 (d, 2H, Ar_{bzim}-H), 8.44 (s,1H, NCHN). Anal. Cal. For $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45 %, found: C, 80.08; H, 5.64; N, 12.97 %.

Synthesis of complexes:

a- *Synthesis of diaquabis(1-benzylbenzimidazole)oxovanadium(IV)* (**1**)

In this experiment, V_2O_5 used as starting material for vanadium, so it has been converted to VO^{+2} ($VOSO_4$) using H_2SO_4 as reducing agent. Then, 1 gm of the ligand dissolved in 10 ml of ethanol was added to a solution of 0.4 g of $VOSO_4$ in 5 ml of ethanol. The reaction mixture was heated at 50-60 ^{o}C with constant stirring for 1 hr and left standing for 1 day. Then, the solution was neutralized with diluted sodium carbonate (20 ml) to get the precipitate as pale green solid. The precipitate was filtered and washed with ethanol and distilled water. The yield percentage was 62 %. Anal. Cal. for $C_{28}H_{28}N_4SO_7V$: C, 54.63; H, 4.58; N, 9.10 %, found: C, 53.89; H, 4.73; N, 8.44 %

b- Synthesis of dinitratobis(1-benzylbenzimidazole)cobalt(II) nitrate (2):

To a solution of the ligand 0.8 g dissolved in 10 ml of ethanol, 0.12 g of $Co(NO_3)_2.2H_2O$ dissolved in 5 ml of ethanol, was added. The mixture was heated to 50-60 ^{o}C for 1 h with constant stirring. The resulted light blue precipitate was filtered and washed with ethanol and distilled water. The yield percentage was 74 %. Anal. Cal. for $C_{28}H_{24}N_6O_6Co$: C, 56.10; H, 4.04; N, 14.02 %, found: C, 55.87; H, 3.73; N, 13.65 %.

c- Synthesis of dichlorobis(1-benzylbenzimidazole)Nickel(II) (3):

This complex was prepared according to the above-mentioned procedure for cobalt complex, except using 0.23 g of $NiCl_2.6H_2O$ instead of $Co(NO_3)_2.2H_2O$. The yield percentage of resulted light green precipitate was 81 %. Anal. Cal. for $C_{28}H_{24}Cl_2N_4Ni$: C, 61.58; H, 4.43; N, 10.26 %, found: C, 61.33; H, 4.09; N, 9.72 %.

e- Synthesis of dinitratobis(1-benzylbenzimidazole)Copper(II) nitrate (4):

This complex was prepared according to the above-mentioned procedure for cobalt complex, except using 0.18 g of $Cu(NO_3)_2$ instead of $Co(NO_3)_2.2H_2O$. The yield percentage of resulted light blue precipitate was 67.7 %. Anal. Cal for $C_{28}H_{24}N_6O_6Cu$: C, 55.67; H, 4.00; N, 13.91 %, found: C, 55.12; H, 3.82; N, 13.32 %.

f- Synthesis of bis(1-benzylbenzimidazole)silver(I) nitrate (5):

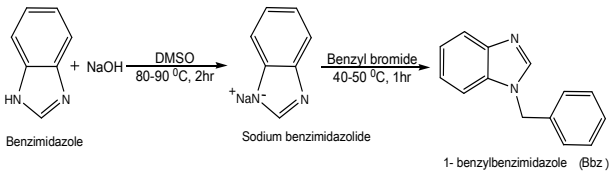
This complex was prepared according to the above-mentioned procedure for cobalt complex, except using 0.3 g of $AgNO_3$ instead of $Co(NO_3)_2.2H_2O$. The yield percentage of resulted pale yellow precipitate was 53 %. Anal. Cal. For $C_{28}H_{24}N_5O_3Ag$: C, 57.35; H, 4.13; N, 11.94 %, found: C, 56.85; H, 3.94; N, 12.44 %.

RESULTS AND DISCUSSION

Synthesis of the ligand (Bbz):

The ligand 1-benzylbenzimidazole (Bbz) was synthesized as described in Scheme 1. Arylation of benzimidazole was performing by two continuing steps. Firstly, benzimidazole was converted to sodium benzimidazolide by reaction with NaOH in DMSO at 80-90 ^{o}C for 2hrs. Secondly, benzyl bromide was added with vigorous stirring to the mixture after cooling to 40-50 ^{o}C. After 1 hr, the mixture was poured in cold water to give the ligand

as a beige precipitate in 87 %. The ligand was soluble in most organic solvents like methanol, ethanol, acetonitrile and DMSO while it was insoluble in diethyl ether and water.



Scheme 1: Synthesis of the ligand 1-benzylbenzim- idazole (Bbz)

Synthesis of metal complexes (1-6):

The reaction of ligand (Bbz) with the selected metal sources produced the metal complexes in different colors and 53-81 % yield percentage. In complex 1, V_2O_5 was used as vanadium source, which is then converted to VO^{+2} using H_2SO_4 in ethanol and then reacted with the ligand. Neutralization of the solution using diluted sodium carbonate solution produced the desired product in satisfied yield. Other complexes were prepared by direct reaction of the ligand (Bbz) with suitable metal sources in warmed ethanol.

^{1}H NMR spectrum:

The ^{1}H NMR for the prepared ligand (Bbz) was recorded in DMSO-d_6 over the scan range 0-16 δ ppm. The compound showed the common signals for 1-substituted benzimidazole. The benzylic proton signal appears at δ 5.49. The multiple bands that appeared in the range δ 7.17-7.44 are belong to five protons of the benzene ring. The protons of fused benzene ring in benzimidazole appeared as two bands, the first one appeared as a triplet at δ 7.5, while the second one appeared as a doublet at δ 7.64. Finally, the signals of NCHN proton appeared at δ 8.44 as singlet peak. The ^{1}H NMR spectrum of the ligand is shown in Figure 1.

Electronic spectra:

Uv-visible spectra of ligand showed two peaks in the range 290-350 nm. These peaks are due to π→π* transition of benzimidazole and benzene ring (Yousif *et al*., 2010). In the complexes, the mentioned peaks were shifted to higher wavelength (red shift), which is an evidence for complexation with the metal. The d→d transitions for the complexes are of little help in the present case, since they are masked by the broad strong charge-transfer bands in the range 430-550 nm. Uv-vis spectra of the ligand and selected complexes are shown in Figures 2, 3 and 4.

Infrared spectra:

In FT-IR spectrum of the ligand (Bbz), the two strong and sharp stretching vibrations in the range 3440-3385 cm^{-1} are due to the tertiary nitrogen module =N-CH_2-Ar of benzimidazole ring. The C-H stretching vibrational bands of both aromatic and methylene (N-CH_2-Ar) group appeared at around 3200-2900 cm^{-1}. The strong sharp peak which appeared at 1398 cm^{-1} is due to the stretching of –CH=N- module of benzimidazole ring (Hranjec *et al*., 2011). Another band of medium intensity in the range 1560–1590 cm^{-1}, which is assigned to benzimidazole ring ν(C=N) vibrations (Galal *et al*., 2009). The bending of aromatic C-H appeared as strong and sharp peaks in the range 800-640 cm^{-1}.

In complexes spectra, many of bands that appeared in the ligand spectrum appeared in its corresponding metal complexes spectra, but, in different forms, intensities, and positions. In general, the peak due to the tertiary nitrogen which appeared at 3440-3385 cm^{-1} became very weak. This is indicating to the formation of metal complexes with the ligand which possibly occurs via imine nitrogen atom (Yoe-Reyes *et al*., 2005). Infrared spectra of the ligand and selected complexes are shown in Figures 5, 6, 7 and 8.

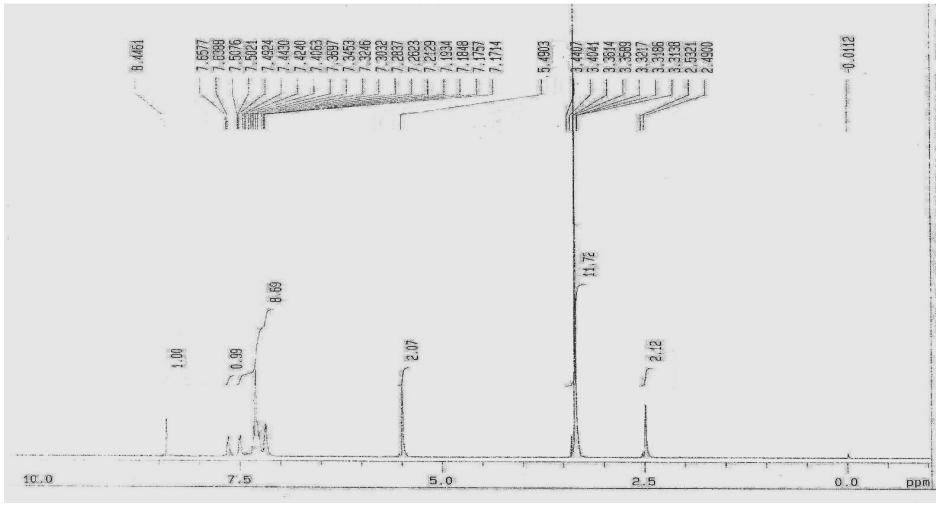


Fig. 1: ^{1}H NMR spectrum of the ligand Bbz in d_6-DMSO.

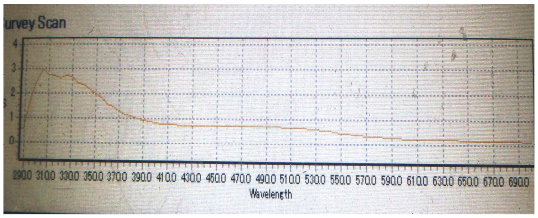


Fig. 2: Uv-vis spectrum for the ligand (Bbz).

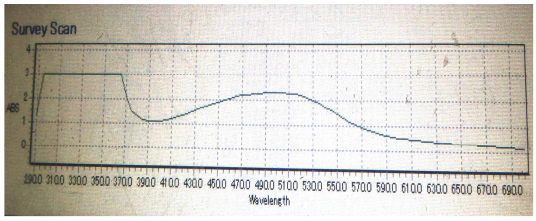


Fig. 3: Uv-vis spectrum for Co^{+2} complex.

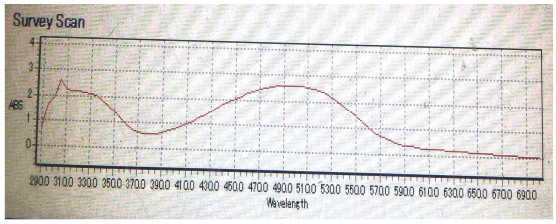


Fig. 4: Uv-vis spectrum for Ni^{+2} complex.

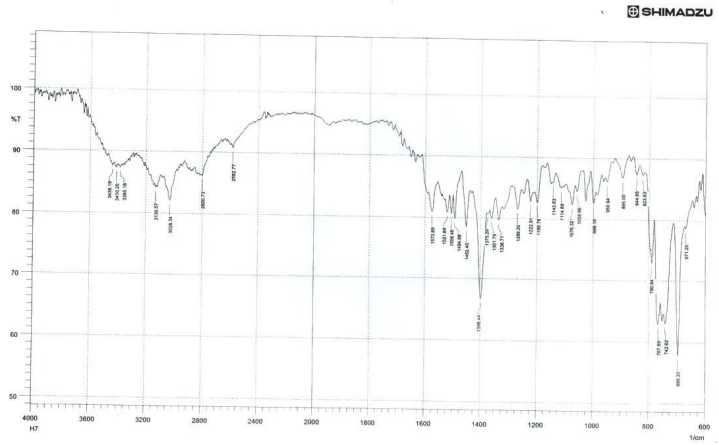


Fig. 5: Infrared spectrum for the ligand (Bbz).

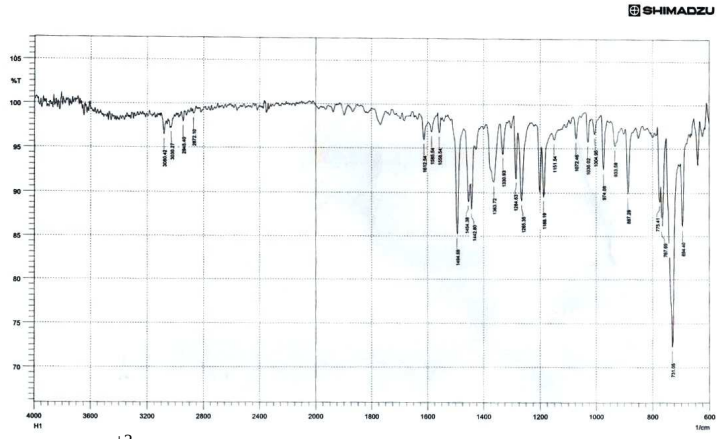


Fig. 6: Infrared spectrum for VO^{+2} complex.

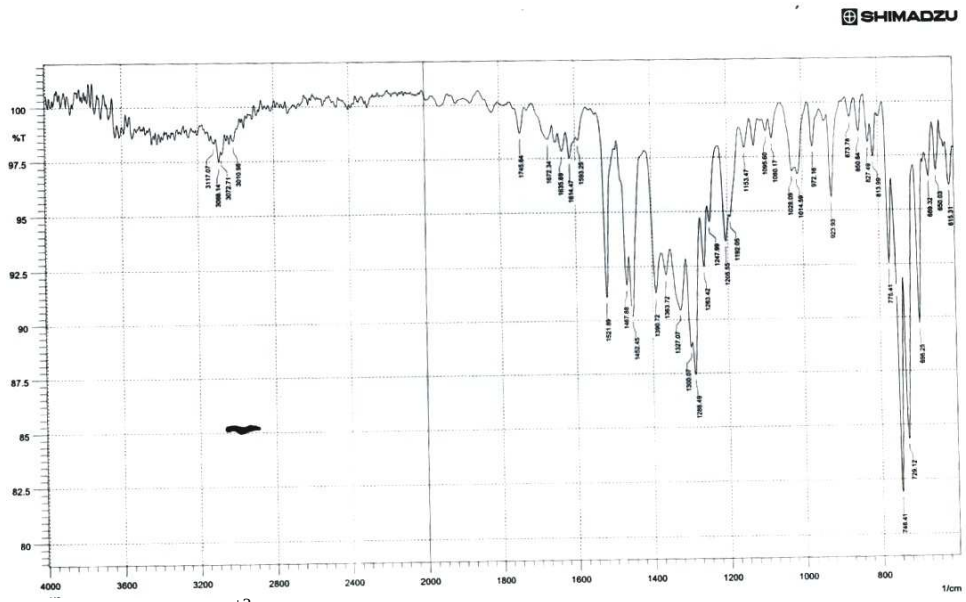


Fig. 7: Infrared spectrum for Cu^{+2} complex.

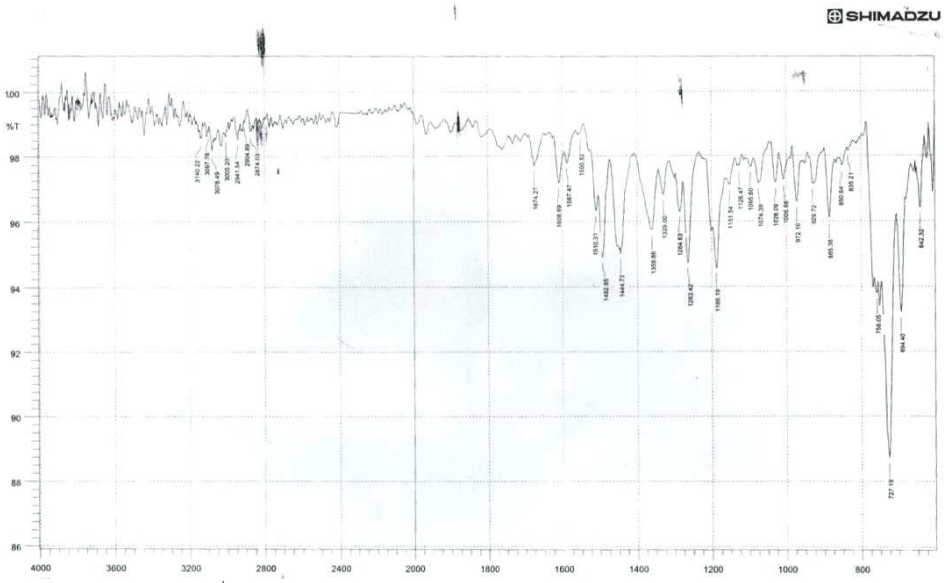


Fig. 8: Infrared spectrum for Ag^{+} complex.

Proposed structures:

Several studies have reported cobalt(II) and zinc(II) coordination compounds showing a similar stoichiometry ($M(bz)_2X_2$) (M^{II} = Co, Zn; X^- = Cl, Br, I), (bz = benzimidazole) (Fabiola *et al*., 2008). In all cases, the geometry adopted by the metal ion is tetrahedral (Figure 9). The metal center is bonded to two halides and two benzimidazole ligands. The benzimidazoles are bonded through the nitrogen of imine group (Yoe-Reyes *et al*., 2005).

Copper(II) complexes presented different behavior, as in ($Cu(bz)_2Br_2$) complex (Figure 10). In this complex, the Cu(II) ion adopted a trans-square planar geometry, to minimize the steric hindrance of the benzimidazole molecules (Bukowska-Strzyzewska and Tosik, 1991).

Depending on the previous studies, and the experimental, analytical and spectroscopic data in this study, the structures in Figure 11 were proposed.

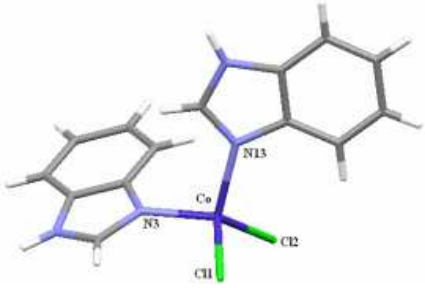


Fig. 9: The complex Dichloro-bis(1H-benzimidazole)-cobalt(II) in a tetrahedral geometry.

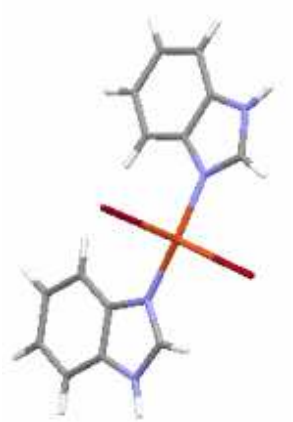


Fig. 10: The complex Dichloro-bis(1H-benzimidazole)-copper(II) in square planar geometry.

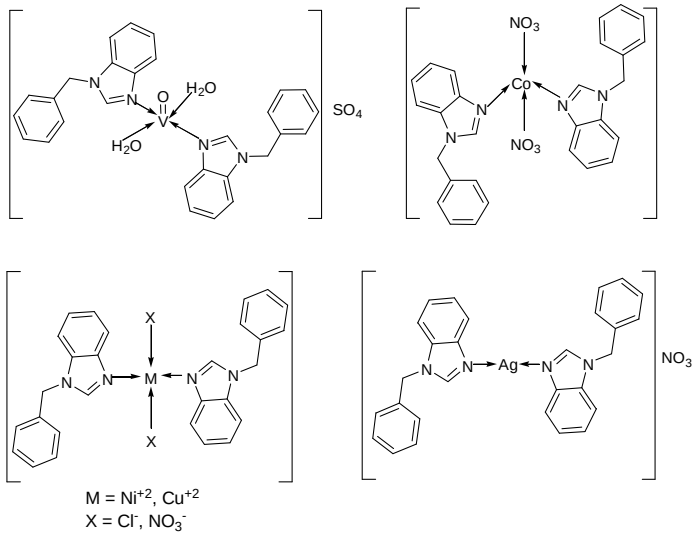


Fig. 11: Proposed structures for the prepared complexes.

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