

NEW MONO- and Bi-NUCLEAR SCHIFF BASE METAL COMPLEXES AND THEIR REACTION WITH HYDROGEN PEROXIDE

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Abstract

The reaction with two Schiff base ligands produced novel complexes of cobalt (II), nickel (II), and copper (II) salts in both neutral and basic environments. Salicylaldehyde was condensed with benzoyl hydrazine (SBH₂) and salicylohydrazine to make the ligands (SSH₃). Elemental analysis, conductivity, infrared, electronic absorption spectra, and magnetic moment measurements were used to characterize the complexes of the generic formulas [M(SBH₂) X₂]₂ [M(SSH₃) X₂], K₂[M(SB)X (H₂O)]₂ and K [M (SS) (H₂O)]₂. The results show a 1:1 metal to ligand ratio, non-electrolytic nature for neutral medium complexes, 1:2 and 1:1 electrolyte for SBH₂ and SSH₃, and non-electrolytic nature for basic medium complexes. According to the investigations, all of the complexes had anionic bridges and octahedral geometry. Some of these complexes' stability constants and reactions with hydrogen peroxide were measured spectrophotometrically.

Keywords: Complexes, Ligands, Metals, Schiff bases.

Introduction

The catalytic activity of various metal complexes has been studied using the breakdown of hydrogen peroxide as a model process. It has also been researched as a catalase model (1-7), despite the catalytic mechanism not being fully explained. Many metal ions have been recognized for over a century to dramatically accelerate the breakdown of H₂O₂ to H₂O and O₂ (4-9). Metal II complexes have been studied extensively, particularly with diverse ligands functioning as catalysts, and debates over mechanistic details involving intermediate radicals or complexes have lingered for decades (10-11). The decay of peroxides was shown to accelerate when metal ions such as copper or ferric ions were added (12). In general, complexes that cause a decrease in the extent of oxidation during their reaction with hydrogen peroxide can be used as radioprotectants, whereas complexes that cause an increase in the extent of oxidation during or after exposure to ionizing radiation can be classified as radiosensitizers [13]. The significance of this behavior is to reduce the influence of radiation dose on the healthy tissue surrounding cancer, which is easily affected when radiotherapy is used to treat malignant disorders.

This paper describes the synthesis and characterization of certain metal II Schiff base complexes. Spectrophotometric analysis of the interaction of certain of these complexes with hydrogen peroxide revealed that superoxide molecules develop in solution and solid-state.

Materials and Methods:

The chemicals utilized in this project were of Analar grade and were employed as-is, with no further purification. Following conventional technique, benzoyl- and salicyloylhydrazines were made by reacting hydrazine hydrate with the respective esters (14). The Schiff base ligands were made by equimolar condensation of the hydrazides and salicylaldehyde produced above in pure ethanol. For around 2 hours, the reaction mixture was refluxed in a water bath. The precipitated ligands were filtered off after cooling, washed with cold ethanol, and dried. SBH₂ has a melting point of 196 °C (yield 82%), while SSH₃ has a melting point of 252 °C. (yield 81percent). Elemental analysis IR spectra (Table 2) and ¹H NMR spectral measurements were used to describe these ligands.

Preparation of the complexes:

The following general approach was used to prepare the complexes. A heated ethanolic solution (15 ml) of the ligand was mixed with a solution of the metal salt in ethanol (10–15 ml) (a 1:1 metal to ligand ratio was always used). The resulting combination was then subjected to two distinct treatments:

i. The mixture was refluxed for around 30 minutes in a water bath, and after it cooled, lovely colored crystals separated out.

The aforementioned combination was treated with a 0.1M ethanolic potassium hydroxide solution until complete precipitation occurred at pH 8.5 – 9.0. The resulting mixture was digested for a few minutes in a water bath before being chilled.

Both methods' isolated complexes were filtered, washed with ethanol, and dried in vacuo on calcium chloride.

The reaction of the complexes with hydrogen peroxide:

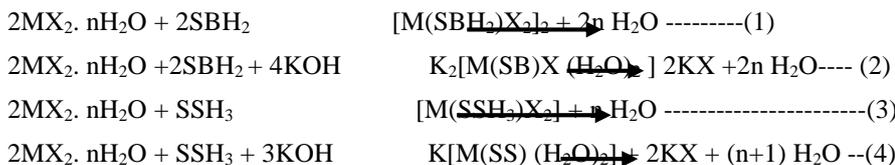
For the spectrophotometric research, a 1:10 (V/V) mixture of 1×10^{-3} M of each complex (dissolved in dimethylformamide DMF) and H_2O_2 (diluted with 100% ethanol and standardized by the iodide method) was utilized. Time was used to track the decline of the absorption peaks at 380 nm.

Analysis and physical measurements:

Using an 1106 carol Erba microanalyzer, carbon, hydrogen, and nitrogen were examined for the ligands and their complexes. The metal was determined using the atomic absorption technique on a Perkin-Elmer instrument (Model A 60). An electrolytic conductivity bridge model LF-42 evaluated conductivities for a 10^{-3} M solution in DMF. KBr pellets and nujol granules were used to record infrared absorption spectra on a Pye-Unicam SP 2000 ($200-4000\text{ cm}^{-1}$) spectrophotometer. Shimadzu UV-160 spectrophotometers were used to record electronic spectral measurements in DMF spanning the concentration range of $10^{-3}-10^{-5}$ M using a 1 cm^3 quartz cell. The $^1\text{H NMR}$ spectra were recorded using TMS as an internal reference on a Perkin-Elmer (A-60) spectrometer. The magnetic susceptibility measurements were performed using a Bruker BM_6 device and the Faraday method. Pascal's constant (15) was used to determine diamagnetic adjustments.

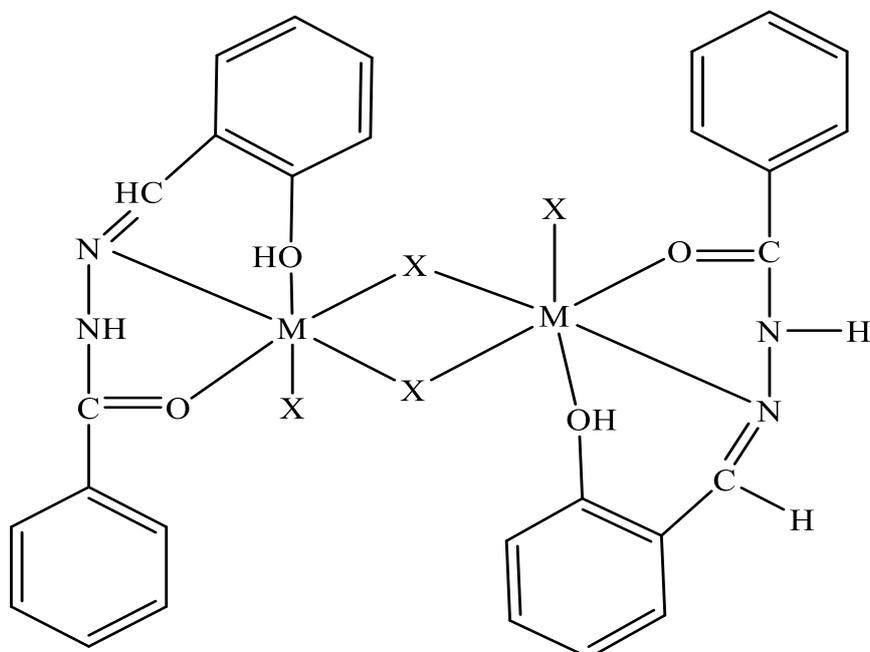
Results

The following equations could be used to describe the production of complexes in both neutral and basic media (1-4).

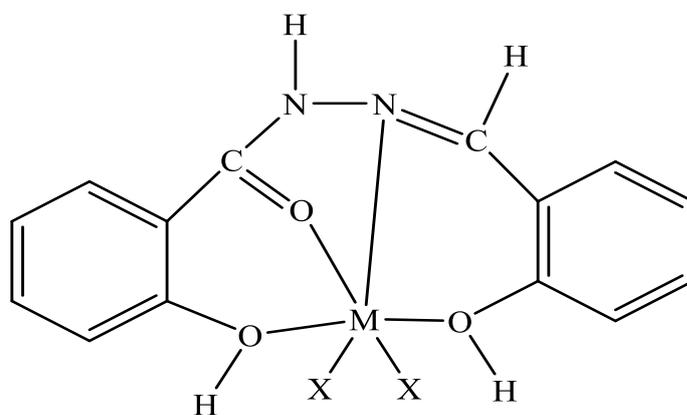


Where $\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$; $\text{X} = \text{Cl}$ or NO_3 ; $\text{SBH}_2, \text{SSH}_3$ are the neutral ligands, while SB, SS are the di and tribasic ligands, respectively. Neutral and anionic complexes were produced for both types of reactions, as illustrated in the preceding equations. Molar conductance measurements in DMF (16) verified this (Table1). The analytical data for the ligands and their complexes (Table 1) correlate well with the supplied formulations and reveal that all complexes have metal to ligand ratio of 1:1. This was also accomplished by utilizing the mole-ratio approach to estimate the reaction components (17). The complexes are relatively stable in dry air, but moisture causes them to disintegrate very slowly. Water is insoluble for all of the complexes; however, they are marginally soluble in DMF, ethanol, and methanol. SSH_3 complexes are marginally more stable than SBH_2 complexes, according to the assessment of the stability constant in absolute ethanolic solution for certain of them Table 1. This could be owing to the existence of a fourth coordination site in the SSH_3 ligand, as opposed to three in the SBH_2 ligand (Fig. 1).

Compound	Yield (%)	$\lambda_m(\text{DMF})(\text{cm}^2 \text{ ohem.mol}^{-1})$	solubility constant (K)	Analysis %		Calculated (found)	
				C	H	N	M
$[\text{Co}(\text{SBH}_2)\text{Cl}_2]_2$	78	12	2.3×10^4	45.62(45.41)	3.36(3.24)	7.81(7.57)	16.10(15.95)
$[\text{Ni}(\text{SBH}_2)\text{Cl}_2]_2$	80	16	3.1×10^4	45.21(45.41)	3.10(3.24)	7.62(7.52)	15.83(15.96)
$[\text{Cu}(\text{SBH}_2)(\text{NO}_3)_2]_2$	83	9	..	38.58(38.36)	2.88(2.74)	13.02(12.79)	14.50(14.61)
$[\text{Co}(\text{SSH}_3)\text{Cl}_2]$	82	14	..	43.36(43.52)	3.31(3.11)	7.45(7.25)	15.42(15.29)
$[\text{Ni}(\text{SSH}_3)\text{Cl}_2]$	91	18	4.2×10^5	43.68(43.52)	3.38(3.11)	7.53(7.25)	15.62(15.29)
$[\text{Cu}(\text{SSH}_3)(\text{NO}_3)_2]$	84	10	3.8×10^5	37.21(37.00)	2.80(2.64)	12.45(2.33)	14.13(14.09)
$\text{K}_2[\text{Co}(\text{SB})\text{Cl}(\text{H}_2\text{O})]_2$	86	140	4.2×10^5	43.46(43.30)	2.86(3.09)	7.18(7.22)	15.37(15.21)
$\text{K}_2[\text{Ni}(\text{SB})\text{Cl}(\text{H}_2\text{O})]_2$	80	152	3.6×10^5	43.12(43.31)	3.12(3.10)	7.43(7.23)	15.18(15.22)
$\text{K}_2[\text{Cu}(\text{SB})\text{NO}_3(\text{H}_2\text{O})]_2$	82	148	..	40.28(40.00)	2.79(2.86)	10.30(10.00)	15.45(15.24)
$\text{K}[\text{Co}(\text{SS})(\text{H}_2\text{O})_2]$	77	96	..	43.55(43.41)	3.60(3.36)	7.10(7.24)	15.38(15.25)
$\text{K}[\text{Ni}(\text{SS})(\text{H}_2\text{O})_2]$	81	102	6.1×10^6	43.22(43.42)	3.38(3.37)	7.42(7.25)	15.46(15.25)
$\text{K}[\text{Cu}(\text{SS})(\text{H}_2\text{O})_2]$	84	110	4.9×10^6	42.58(42.86)	3.21(3.32)	7.34(7.14)	16.18(16.33)



SBH₂-Complexes



SSH₃-Complexes

M=Co⁺², Ni⁺², Cu⁺² and X=Cl⁻ or NO₃⁻

Infrared spectra:

By comparing the infrared absorption spectra of the free ligands and their complexes, the coordination sites of the ligands were deduced. Table 2 shows the major infrared bands of the ligands and their complexes. The findings for complexes produced in a neutral medium revealed a negative shift in the bands due to OH, C=O, and C=N vibrations, demonstrating that the ligands are coordinated in their neutral state (18,19). The lines related to OH, NH, and C=O, on the other hand, were absent from the spectra of complexes produced in basic solution, indicating that the ligands in their anionic forms were coordinated (20). M-N and M-O modes were seen in the spectra of all compounds around 420-430 and 440-450 cm⁻¹, respectively (21). In addition, two bands occurred in the range 325 and 350 cm⁻¹, which were ascribed to the cis form's terminal M-Cl modes. Bridging M-Cl vibration is responsible for the band at 310 cm⁻¹ (22). Furthermore, the infrared bands at 1430, 1310, and 1010 cm⁻¹ are attributed to N-O stretching vibrations of unidentate nitrate group coordination (21, 22). The bands about 1470, 1280, and 1020 cm⁻¹, on the other hand, are tentatively assigned to the bridging NO₃ group (21). Stretching and rocking bands at 3500 and 970 cm⁻¹, respectively, were used to define coordinated water (23).

Table 2. Important IR spectral bands (cm⁻¹) for ligands and their complexes

Compound	VOH	VSH	VC=O	VC=N	VOH	VN=N	VC=O	VM-N	VM-O
SBH2	3300	3160	1670	1630	1290	1010	1210
SSH2	3300	3150	1680	1630	1290	1010	1210
[Co(SBH2)Cl2]2	3180	3150	1640	1600	1260	1020	1190	420	445
[Ni(SBH2)Cl2]2	3190	3150	1445	1605	1265	1020	1180	430	440
[Cu(SBH2)(NO3)2]2	3190	3150	1650	1605	1265	1025	1180	430	440
[Co(SSH3)Cl2]	3200	3150	1650	1600	1270	1020	1180	425	440
[Ni(SSH3)Cl2]	3200	3150	1650	1595	1265	1020	1185	425	450
[Cu(SSH3)(NO3)2]	3190	3150	..	1600	1265	1025	1190	420	450
K2[Co(SB)Cl(H2O)2]	1605	..	1025	1185	425	445
K2[Ni(SB)Cl(H2O)2]	1600	..	1025	1185	425	440
K2[Cu(SB)NO3(H2O)2]	1600	..	1020	1185	430	440
K[Co(SS)(H2O)2]	1605	..	1030	1190	430	450
K[Ni(SS)(H2O)2]	1605	..	1185	425	450	..
K[Cu(SS)(H2O)2]	1605	..	1025	1185	430	445

Electronic spectra and magnetic moments:

All DMF complexes' electronic spectra showed suitable transitions corresponding to the bipovalent cobalt, nickel, and copper cations (Table 3). The spectra of cobalt (II) complexes showed only two bands due to v_1 and v_2 of ${}^4T_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively. The v_3 band of ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition is very weak and could not be observed [17].

The spectra of nickel (II) complexes showed three bands, v_1 , v_2 and v_3 , due to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively.

The electronic spectra of copper (II) complexes showed only one broadband due to the three combined transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, and ${}^2B_{1g} \rightarrow {}^2E_g$. The number and position of these bands agree with the octahedral geometry of these complexes [24]. Table 3 shows the magnetic moments of the compounds. The results revealed that all of the complexes are paramagnetic, with three, two, and one unpaired electrons, respectively, for cobalt (II), nickel (II), and copper (II) complexes. The antiferromagnetic interaction that occurs through the chloride bridges causes a minor divergence (lower value) from the spin-only moment for the dinuclear complexes. Binuclear complexes generated through nitrate bridges on the other bands exhibited no variation from the spin-only values. The small M-L and long M-M distances created by bridging through polyatomic anions are responsible for this (25,26).

Table 3. Magnetic moments and electronic spectral data

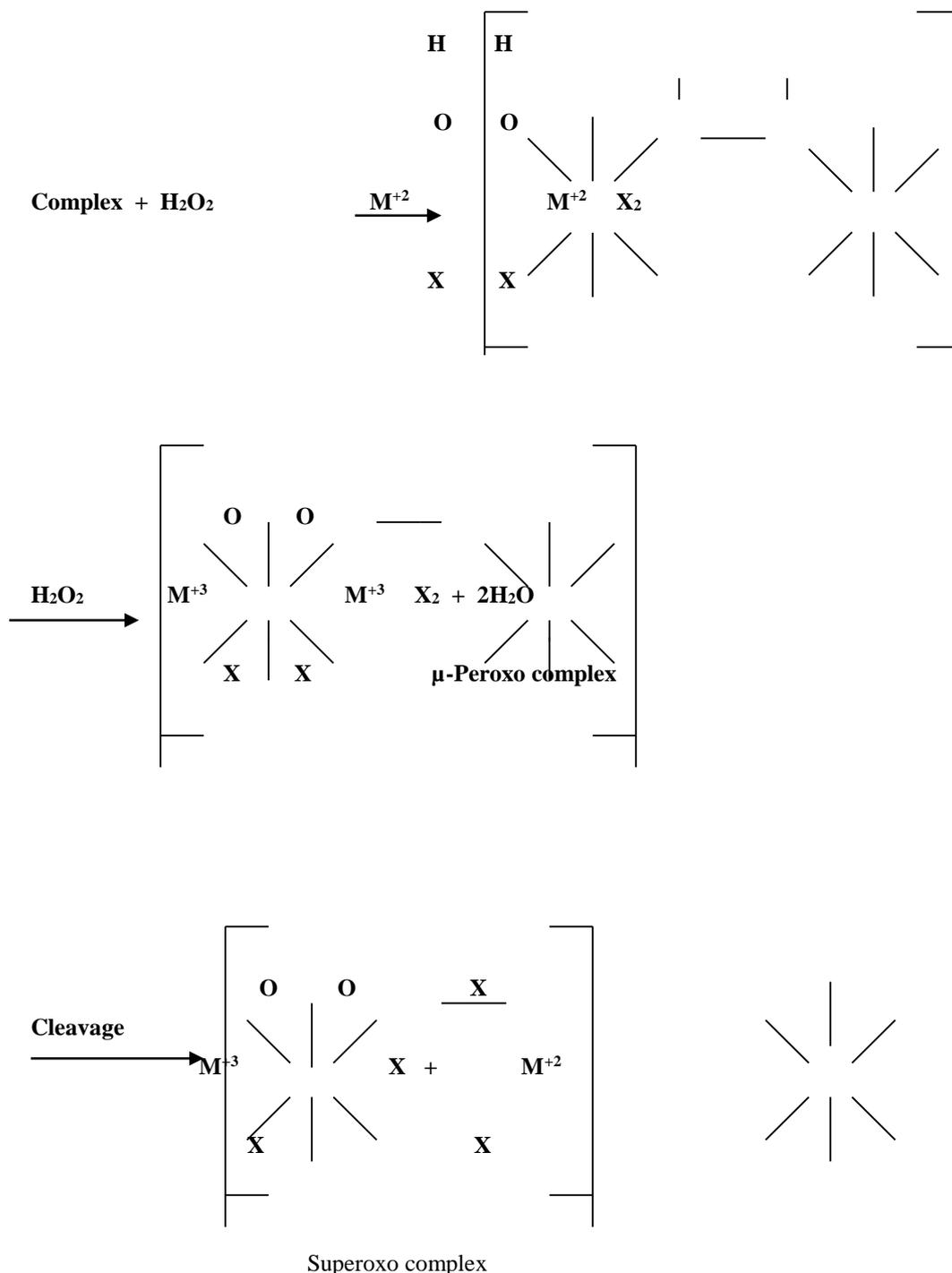
Compound	μ_{eff} (B.M)	v_1	v_2	v_3
[Co (SBH ₂) Cl ₂] ₂	3.62	9800	-	22400
[Ni (SBH ₂) Cl ₂] ₂	2.61	10100	16400	26350
[Cu (SBH ₂)(NO ₃) ₂] ₂	1.54	14600	-	-
[Co (SSH ₃) Cl ₂]	4.21	10100	-	21900
[Ni (SSH ₃) Cl ₂]	2.92	10150	16300	26400
[Cu (SSH ₃)(NO ₃) ₂]	1.80	14350	-	-
K ₂ [Co (SB)Cl(H ₂ O) ₂] ₂	3.54	10150	-	22100
K ₂ [Ni (SB)Cl(H ₂ O) ₂] ₂	2.52	9800	16100	27100
K ₂ [Cu (SB)(NO ₃)(H ₂ O) ₂] ₂	1.50	13800	-	-
K[Co (SS)(H ₂ O) ₂]	4.30	9900	-	21800
K[Ni (SS)(H ₂ O) ₂]	2.84	10100	11300	26350
K[Cu (SS)(H ₂ O) ₂]	1.78	14100	-	-

Reaction with hydrogen peroxide:

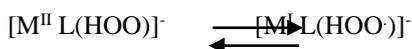
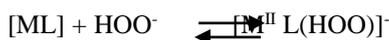
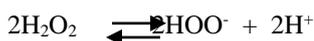
For hydrogen peroxide production, various mechanistic mechanisms have been proposed [27, 28]. Metal ions or metal complexes can catalyze the disproportionate reaction. The production of an OH radical, as seen in the reaction of H₂O₂ with ferrous salts [29], has been proposed as one probable mechanism.

Hydrogen peroxide reacts with some of the prepared complexes was studied spectrophotometrically. The addition of H₂O₂ to a solution of the complexes results in a decrease in the intensity of the absorption maxima of the charge transfer band in the UV region with the development of a new band at about 330 nm. This was attributed to the formation of superoxocompounds that usually show an intense absorption in the range of 310-340 nm [30]. The formation of such species usually requires the oxidation or reduction of the metal ion to the trivalent or univalent states [11,31,]. The formation of superoxo compound results from the decomposition of μ-peroxo intermediate formed through the addition of H₂O₂, as shown in scheme 1.

The following mechanism represents the oxidation process:



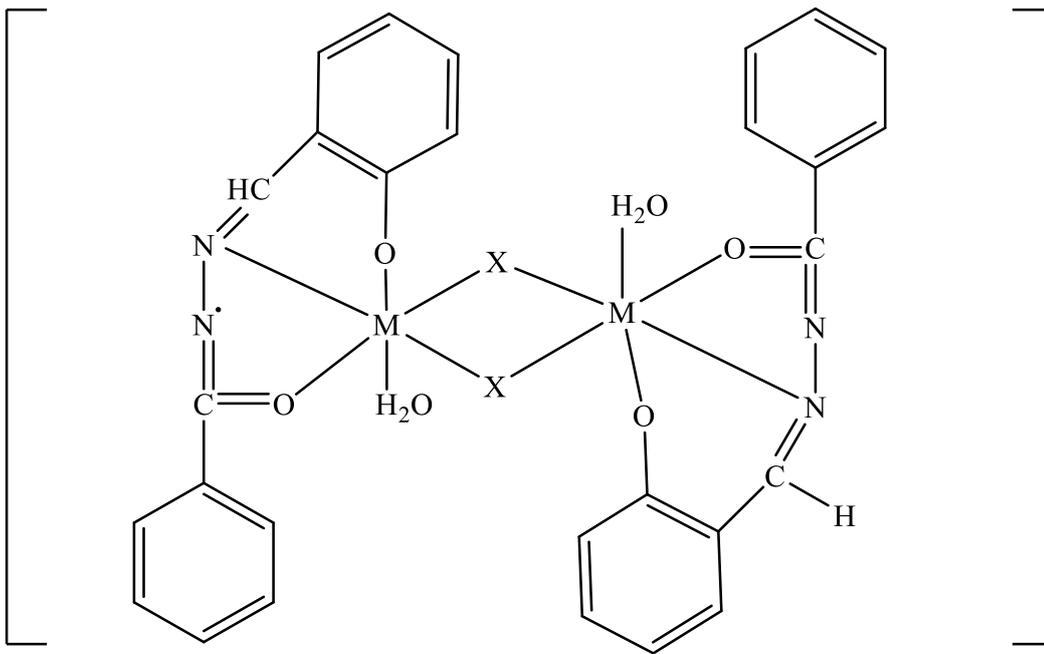
While the reduction process could be represented as follows:



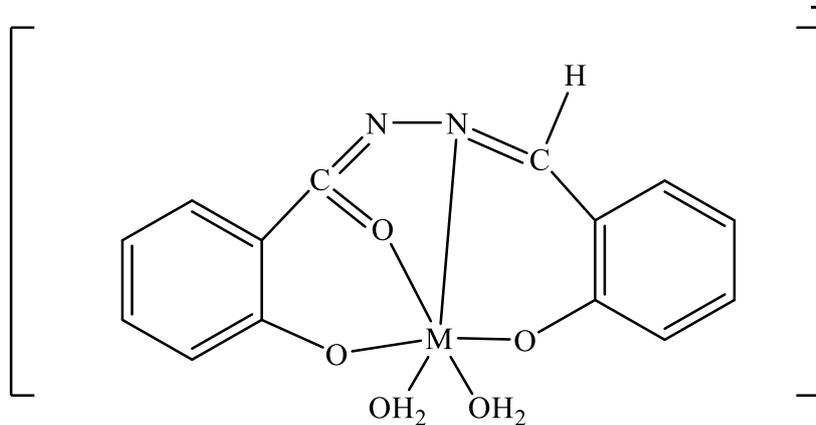
Conclusion

The superoxo species produced in this way was considered stable since the conditions (polar solvent, low temperature, low concentration, and bulky ligands) required for stability were satisfied [36]. It was noticed that the original complex regenerated again within the time, as found from the development of the original charge transfer band. Accordingly, the complex can act as a catalyst that is reformed successfully after the decomposition of H_2O_2 and retains its original structure. Two reactions of the system complex + H_2O , the first with phenolphthalein reagent and the second with diazotization, confirmed the latter action.

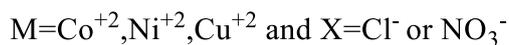
The structures indicated in Figures 1 and 2 have been postulated for all complexes based on the preceding physicochemical and spectral analyses. In these structures, the ligands act as neutral tridentate (SBH_2) and tetradentate (SSH_3) in neutral medium and dibasic (SB) and tribasic (SS) in alkaline solution. In both cases, octahedral geometry for all the complexes was proposed. Since the reaction of these complexes with H_2O_2 increases the extent of oxidation (generate more free radicals), they can be classified as radiosensitizers beside their action as catalysts for certain oxidation reactions.



SB-Complexes



SS-Complexes



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