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# Novel Co(II) metal complexes of N, O donor salicyloylpyrazoleoxime Schiff bases: synthesis, spectroscopic studies and antimicrobial evaluation

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Five novel mononuclear Co(II) chelate complexes derived from salicyloylpyrazoleoximes have been synthesized and characterized using elemental analysis, spectroscopic methods (UV-visible, IR, $^1$H NMR) and thermal analysis. The elemental analysis suggests that the Schiff Base Co(II) complexes have 1:2 stoichiometry. The spectroscopic determination suggest the complexes are square planer and the Schiff base coordinate to Co(II) metal through imine nitrogen and phenolic oxygen. All synthesized complexes are stable, non-hygroscopic, non-electrolytic and amorphous in nature. Most of the ligands and Co(II) complexes possess moderate antimicrobial activity against the test bacteria.

**Keywords:** Co(II) Complexes, Mononuclear, Schiff base, Salicyloylpyrazoleoximes, Antimicrobial activity

Coordination compounds are formed by combining the functionalities of both metal cation and organic anions/molecules as the ligand. The coordination compounds represent hybrid material because they exhibit new properties besides the intrinsic properties of the involved molecular precursors. The coordination chemistry of hydroxyoximes is versatile because it is associated with hydroxyl group in addition to imine functionality and it is used as complexing agent. The hydroxyoximes easily make coordinate bond with bivalent metal through oxygen atom of phenol by deprotonation and through N-atom of imine group. Oximes containing nitrogen and oxygen atom and are potentially ambidentate[1] as they can bind either oxygen[2] or the nitrogen[3,4]. In medicinal chemistry, pyrazole and its derivatives occupies important position because of wide range of biological activities. Pyrazole and its derivatives display antibacterial[5], antimicrobial[6], anti-cancer[7], anti-inflammatory[8], insecticides[9], fungicides[10] and many more activities.

Oximes are most useful ligands, as they can easily form complexes with transition metal ions[11]. Most of transition metal complexes with 2-hydroxyoximes have been synthesized previously and reported their applications in various fields[12,13]. The metal complexes derived from oximes have been used as cerebral and myocardial perfusion imagine agent[14,15]. The oximes have structural features in the metal complexes because of formation of intramolecular hydrogen bonds. This intramolecular hydrogen bonding gives packing configuration which gives rise to important applications as biochemical model[13,17] and semiconducting materials[18,19].

In recent year's number of scientists have tried to find some connection between chemical structure and physiological or biological properties. It is now well-known fact that the activity of a compounds depends upon some factors such as heterocyclic moiety, nature of the substituent and the position of the substituents in these compounds. The study of the chelating ligands associated with oxime group invents from the fact that these types of ligands gives coloured complexes with transition metal ion and showing exciting properties. Transition metal complexes with oxime ligands have attracted much interest because they exhibit excellent coordination ability. Knowledge of their coordination towards metal ion will lead to better understanding of the structure, reactivity and stability of chelate complexes[20,21]. Motivated by the aforementioned findings of hydroxyl oximes, pyrazoleoximes and metal complexes, we conceived our aim to synthesize Co(II) complexes with pyrazoleoximes. In this paper, we describe the synthesis, spectral analysis and microbial activities of novel Co(II) complexes with salicyloylpyrazoleoximes.

## Material and Methods

The ligand salicyloylpyrazoleoxime was synthesized according to our previous method[22]. All the regents and chemicals used were research grade (Merck and Loba Chemicals, More than 99.8% pure). Alcohol and water were distilled prior to use. Infrared spectra were recorded on Schimadzu FT-IR spectrophotometer instrument. UV-visible spectra for the ligand and complexes were recorded on Schimadzu double beam spectrometer (UV-1800). Thermogravimetric analyses were carried in air as atmosphere with heating rate 10 ºC per minute. The percentage of metal in complex was determined by volumetric method[23]. The procedure used for synthesis of complexes was reported in earlier research[24].

### General procedure for synthesis of metal complex

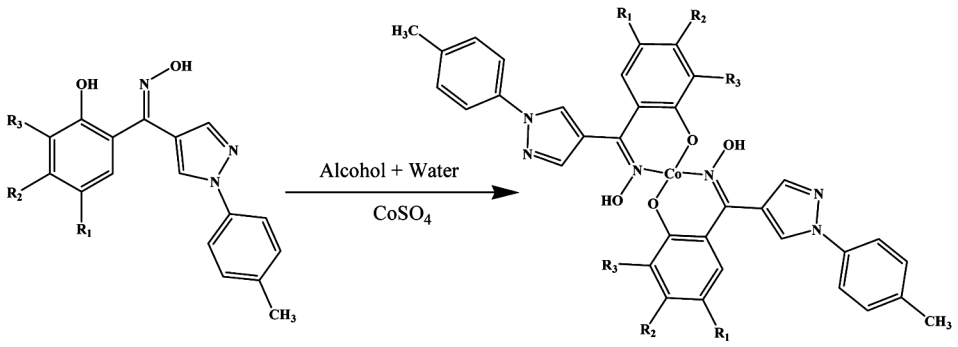
One equivalent of cobalt sulphate (0.001 mol) solution was prepared in distilled water. The metal solution was acidified by concentrated hydrochloric acid. This acidic solution was made warm on hot water bath and then it was further treated with of ethanolic solution of the ligand (0.002 mol). The ligand solution was added slowly drop by drop. A little excess of the ligand solution was added to ensure the complete complexation. This solution was made alkaline using alcoholic ammonia (ethanol + ammonia). The resultant solution was then digested on boiling water bath where coloured precipitate of complex formed. The colored precipitate was filtered, washed with little hot distilled water to remove unreacted metal ion and then by ethanol to remove excess of ligand. The product was dried under ambient conditions. The route for synthesis of Co(II) complex is shown in Scheme 1.

## Result and Discussion

The Co(II) complex with Schiff bases N, O donor substituted salicyloylpyrazoleoxim was synthesized by the reaction of $CoSO_4$ and the ligand in a molar ratio 1:2 (M:L). The elemental analysis data supports for $ML_2$ composition and found to be in agreement with proposed formulae of the complexes. The synthesized complexes are of gray in colours which are different from colour of the ligand. The synthesized metal complexes are non-hygroscopic and stable at room temperature and melts above 200 °C which are different and higher than that of free the ligand. The solubility of complexes was examined in different polar and non-polar solvents. All the complexes are insoluble in water, acetone, chloroform, ethyl alcohol and carbon tetrachloride but only soluble in DMF, DMSO. The analytical data and solubility behaviour of complexes suggest that all the synthesized complexes are monomers. The solution conductivities of synthesized complexes were measured using digital conductivity meter (Elico Model CM-180) in DMF as a solvent. The molar conductivity values for complexes are low indicative non-electrolyte and covalent nature of the complexes[25,26]. This non-electrolyte nature of complexes supports chelating structure in complexes. The physical, analytical and molar conductance values for the synthesized complexes are represented in Table 1.

### IR spectra

In the IR spectra of the ligands broad band in the region 3157–3165 $cm^{-1}$ is observed, which is assignable to hydrogen bonded ν(O-H) stretching frequency. An another absorption band in the region 3223–3430 $cm^{-1}$ assignable to free ν(O-H) stretching frequency. After complexation the frequency in the region 3223–3430 $cm^{-1}$ is due to free hydroxyl group, which was disappeared, which indicates deprotonation followed by the formation of metal oxygen bond of phenolic group. The absorption band in the range 3157–3165 $cm^{-1}$ due to H…O−H was




Scheme 1 — Synthetic route for the synthesis of Co(II) complexes of Salicyloylpyrazoleoxime

also shifted up to lower frequency indicating the coordination of N atom of oxime with metal and presence of strong inter molecular hydrogen bonding between the ligand to stabilize the complex[27,28].

The absorption frequency for C=N and N−O bond was appeared in the region 1541- 1549 $cm^{-1}$ and 1247- 1295 $cm^{-1}$, respectively, in the spectra of the free ligands. The coordination of N atom with metal ion is also evidence by shifting in stretching frequency of azomethine group towards lower value[29,30]. The absorption frequency due to ν(C-O) of phenolic –OH of the free ligand is observed in the 962 – 991 $cm^{-1}$ region. After complexation it showed hypsochromic shift, this supports bonding of the metal ions to the phenolic -OH after deprotonation[31].

The phenolic –OH group and azomethine nitrogen of the ligand coordinate with metal was proved by appearance of new weak bands in the region 531–546 $cm^{-1}$ and 449–465 $cm^{-1}$ which was assigned to ν(M-O) and ν(M-N), respectively[32,33]. These bands are only observed in the spectra of complexes not in the free ligands. Thus all the IR data suggest the metal ion is bonded to salicyloylpyrazole ligand through phenolic oxygen and imino nitrogen atoms[34]. The significant IR frequencies for the ligands and their Co(II) complexes are represented in the Table 2.

**$^1$H NMR spectra**

$^1$H NMR spectrum of the free ligands shows two exchangeable protons and appeared in the range 10–12 ppm. The proton observed near 12 ppm was assigned to intramolecularly hydrogen bonded phenolic –OH group and in spectra of metal complexes it was disappeared. This clearly indicated that the deprotonation of phenolic –OH group involved in coordination with metal ion. The proton signal appeared near the range 10 ppm was assigned to free hydroxyl –OH group of azomethine linkage. This signal was shifted to higher value after complexation. But the chemical shift was small, this indicates that the involvement of nitrogen atom of azomethine linkage to coordinate with metal ion and hydroxyl group forms intermolecular hydrogen bond with other ligand molecule to stabilize the complex. The aromatic methyl groups appeared near 2.4 ppm, aromatic protons appeared in the range 6.5–7.5 ppm and pyrazole protons appeared in the range 8–9 ppm.

Table 1 — Physical and Analytical data of Co (II) complexes

| Complex | Substituents $R_1$ | | | Colour | M. P. (°C) | % Yield | Found (Calcd.) % M | C | H | N | Molar conductance ($\Omega^{-1}$ $cm^2$ $mol^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Co-1 | Cl | H | H | Gray | 202-204 | 85 | 8.13 (8.27) | 57.57 (57.32) | 3.75 (3.68) | 11.99 (11.80) | 29.4 |
| Co-2 | $CH_3$ | H | H | Gray | 264-266 | 79 | 8.58 (8.77) | 64.59 (64.38) | 4.69 (4.80) | 12.38 (12.51) | 15.4 |
| Co-3 | Br | H | H | Gray | 224-226 | 84 | 6.69 (7.35) | 51.19 (50.96) | 3.49 (3.27) | 10.67 (10.49) | 50.0 |
| Co-4 | Cl | $CH_3$ | H | Gray | >300 | 68 | 8.13 (7.96) | 58.11 (58.39) | 3.86 (4.08) | 11.53 (11.35) | 52.3 |
| Co-5 | Cl | H | Cl | Gray | 214-216 | 85 | 7.64 (7.54) | 52.44 (52.26) | 3.47 (3.10) | 10.91 (10.76) | 36.9 |

Table 2 — The significant peaks in FTIR spectra of the free ligand and its Co(II) complexes

| Compound | Frequency ($cm^{-1}$) $\nu_{O-H}$ | $\nu_{C=N}$ | $\nu_{N-O}$ | $\nu_{C-O}$ | $\nu_{M-O}$ | $\nu_{M-N}$ |
|---|---|---|---|---|---|---|
| HL1 | 3364, 3160 | 1541 | 1295 | 985 | - | - |
| Co-1 | 3142 | 1545 | 1233 | 993 | 531 | 461 |
| HL2 | 3244, 3165 | 1548 | 1276 | 962 | - | - |
| Co-2 | 3153 | 1547 | 1230 | 963 | 539 | 458 |
| HL3 | 3223, 3157 | 1548 | 1274 | 991 | - | - |
| Co-3 | 3141 | 1553 | 1232 | 958 | 545 | 465 |
| HL4 | 3430, 3165 | 1549 | 1253 | 985 | - | - |
| Co-4 | 3145 | 1535 | 1251 | 937 | 547 | 449 |
| HL15 | 3264, 3159 | 1551 | 1247 | 971 | - | - |
| Co-5 | 3142 | 1515 | 1233 | 967 | 546 | 461 |

**Powder XRD analysis**

The powder X-ray diffraction of some selected cobalt complexes were obtained in solid form. The X-ray diffractogram of all complexes showed broad peaks, which indicate amorphous nature[35]. Though amorphous nature of complexes was observed they were generally not soluble in non-polar solvents.

**Electronic absorption spectra**

In the present study, UV-visible spectrum of the ligand displays two strong bands in the region 260–340 nm, which are assigned to n→π* and π→π* transitions[36]. The observed $\lambda_{max}$ values for all the synthesized ligands are found to be nearly same. The $\lambda_{max}$ values for the synthesized ligands are represented in Fig. 1.

The UV-visible spectra gave support in establishing geometry of the synthesized metal complexes. In the present investigation due to organic ligands the absorption bands observed in the range 280 nm and 360 nm are attributed to π→π* and n→π* transitions. The shift in absorption frequencies of these bands supports for involvement of oxygen atom of phenol and nitrogen atom of azomethine linkage in coordination with metal. The absorption spectra for Co(II) complexes showed absorption bands in the region 450 – 540 nm which are assignable to charge transfer band suggesting square planar geometry around Co(II) ion[37]. Electronic spectral data of Co(II) complexes were recorded in DMF as solvent and presented in Fig. 2.

**Thermal analysis**

The thermogram of cobalt complexes showed two stage decompositions in the temperature range 220- 800 °C. There is no significant weight loss below 250 °C supports for no lattice or coordinated water molecules in Co-1 and Co-5 complexes and they are highly stable. In Co-1 and Co-5 complexes with salicyloylpyrazoleoximes a significant weight loss begins at 250 °C. The anhydrous compound does not remain stable at higher temperature. The complexes started to decompose slowly, then more rapidly in the range 220- 750 °C with percent weight loss corresponding to decomposition of organic matter. The decomposition completed by leaving air stable residue as CoO obs. % (Cal-10.53 %) for Co-1 and CoO obs. 9.03% (Cal- 9.60%) for Co-5 complexes. The TG plots for selected metal complexes are shown in presented in Fig. 3.

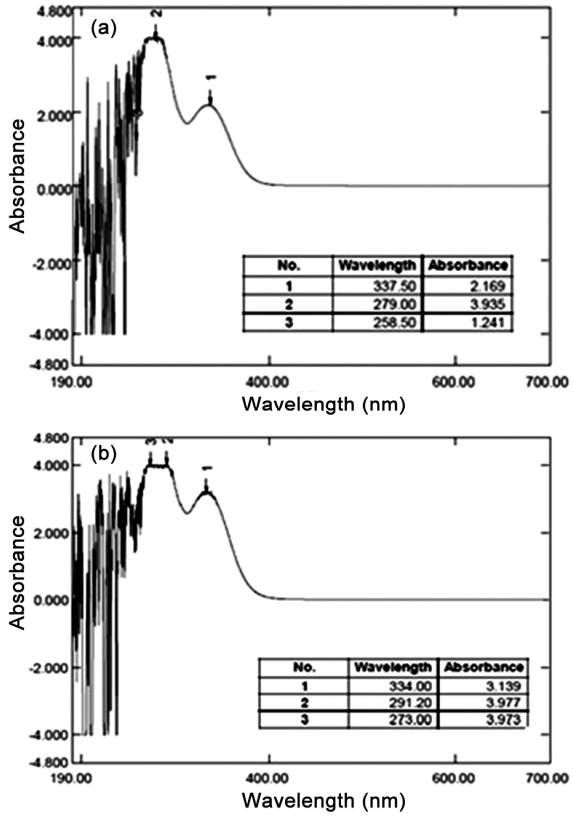



Fig. 1 — Electronic absorption spectrum of the ligand (a) HL2 and (b) HL4

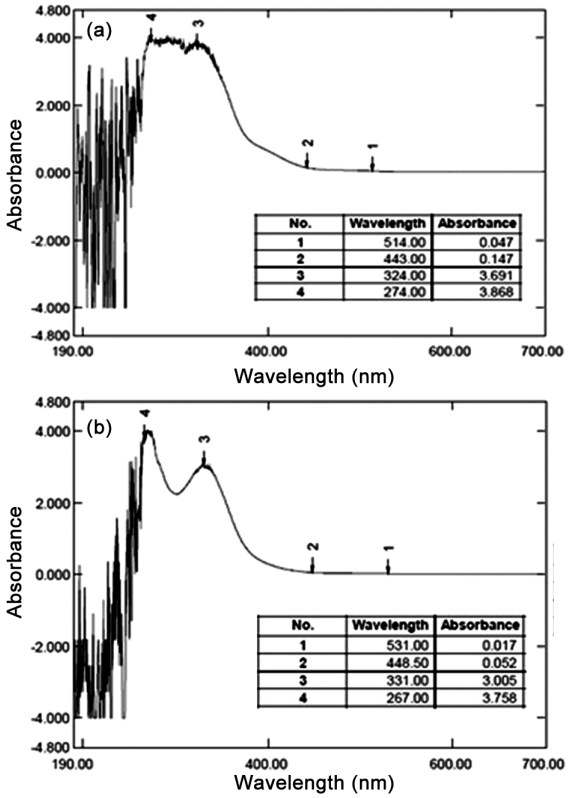



Fig. 2 — Electronic absorption spectra of complex (a) Co-2 and (b) Co-4

**Antibacterial activity**

All the synthesized ligands and cobalt complexes were tested against gram positive bacteria *Bacillus subtilis, Staphylococcus aureus,* Actinomycetes and gram negative bacteria *Klebsiella, Pseudomonas aeruginosa.* The newly synthesized complexes exhibited varying degree of inhibitory effect (low to moderate) on the growth of tested bacteria. The antibacterial data for the synthesized ligand and complexes are presented in Fig. 4.

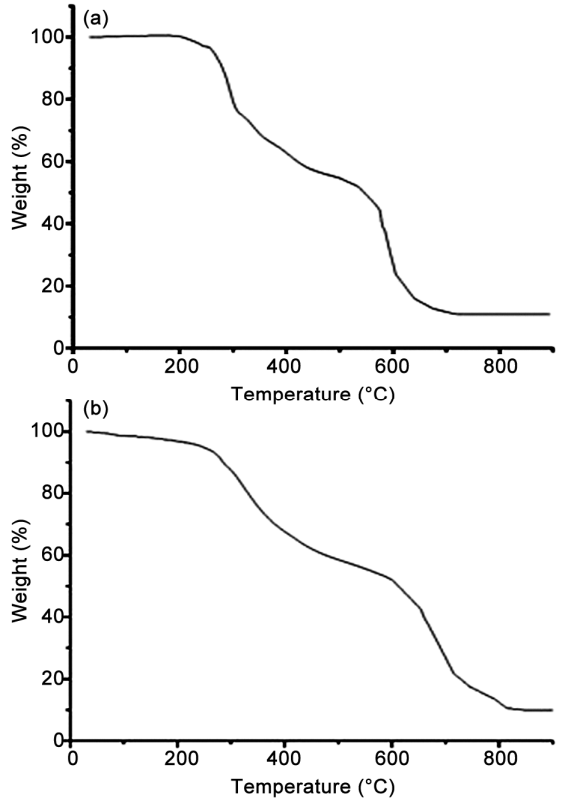



Fig. 3 — TGA plot of complex (a) Co-1 and (b) Co-5

However, in antimicrobial screening the synthesized Schiff base metal complexes were found comparatively much more active than the free ligands. The antimicrobial activity of metal complexes showed considerable zone of inhibition compared to that standard drug Penicillin. Most of the synthesized complexes showed antimicrobial activity against *Actinomycetes* and *Pseudomonas aeruginosa*. After coordination with metal ion, the compounds which are biologically inactive becomes active and biologically less active compounds becomes more active[38,40]. Such introduction and enhancement in the activity of metal complexes were explained on the basis of Overtone's concept[41] and Tweedy's chelation theory[42].

The dissimilarity in the activity of the different metal complexes against different bacteria depends either on the impermeability of the cells of the microbes or difference in the ribosomes in the microbial cells[43,44]. The metal complexes may also be a vehicle for activation of the ligand as a cytotoxic agent. Moreover, complexation may lead to significant reduction of drug resistant[45]. Besides this other factor such as solubility, conductivity and dipole moment influenced by the presence of metal ions may also be the possible reason causing enhancement of the antimicrobial activity of chelate complex as compared to free Schiff base compounds[46]. The antimicrobial activity may also enhance due to involvement of formation of hydrogen bond through the azomethine group with the active centers of cell constituents, resulting in an interference with normal cell process[47].

Now it is clear that, these compounds possess antibacterial properties. Use of these compounds as antibacterial on therapeutic scale need to be further

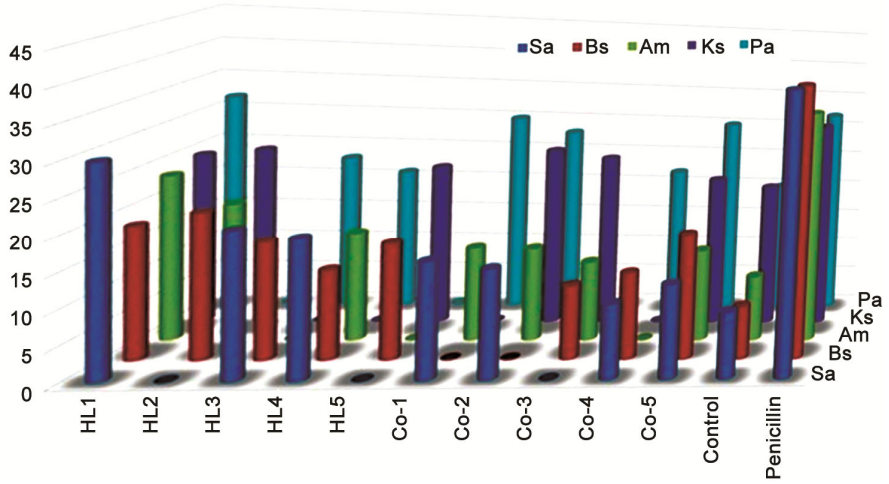



Fig. 4 — Antimicrobial activity of salicyloylpyrazoleoxime and Co(II) complexes

elaborated. In many cases the bacterial pathogens have acquired resistance against traditional compounds or drugs. Under such conditions, these new compounds can be tried as alternative compounds for the control of these pathogens. However, further studies in this direction are needed.

## Conclusions

In this present study, new salycyloylpyrazoleoxime and its cobalt complexes are reported. The formation of metal complexes confirmed by UV-visible, IR and $^1$H NMR spectroscopy. The spectral data suggest that the oxygen atom of phenol group and nitrogen atom of imine group are involved in coordination with metal ion. The formation of metal complexes is also confirmed by thermal methods of analysis. All the metal complexes are stable below 200 °C and decompose slowly after 200 °C giving formation of corresponding metal oxide. The complexes are insoluble in water, alcohol and other organic solvents but good solubility in DMF and DMSO. The electronic absorption spectra suggest probable square planer geometry. The molar conductance values of these complexes suggest the non-electrolytic nature. The antibacterial study revealed that the most of the ligands and metal complexes possess moderate antimicrobial activity.

## Supplementary Data

Supplementary Data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(11)1437-1442_SupplData.pdf.

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