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Synthesis, Spectral, Thermal and Antimicrobial Studies of Cr^{III}, Mn^{II}, Co^{II} and Ni^{II} Complexes of Schiff Base Derived from 4-Aminoantipyrine and 2,4-Dihydroxyacetophenone

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ABSTRACT

Some novel metal complexes of Cr(III), Mn(II), Co(II) and Ni(II) with a Schiff base derived from 4-aminoantipyrine and 2,4-dihydroxyacetophenone have been synthesized and characterized by elemental analyses, molar conductance, IR, electronic spectra, EPR spectra and thermogravimetric studies. The ligand and their complexes were also screened for their possible antibacterial and antifungal activities. The Schiff base ligand behaves as a neutral bidentate chelating agent in all the metal complexes, coordinating through carbonyl oxygen and azomethine nitrogen. All the metal complexes have distorted octahedral geometry.

Keywords: Bidentate Schiff base ligand, 2,4-dihydroxyacetophenone, spectral studies, Thermal studies.

INTRODUCTION

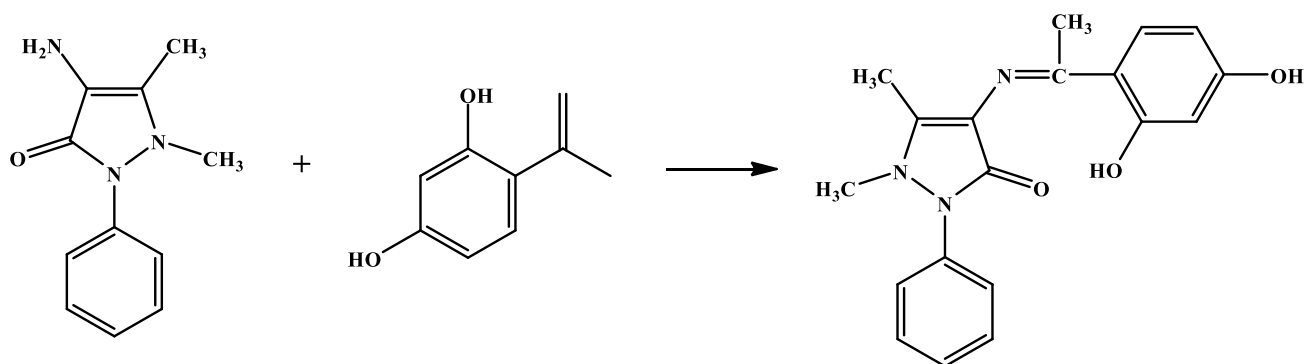
Metal complexes with Schiff base ligand have been subjected of intense investigation for the past several years. The instant and enduring property of Schiff base ligand undoubtedly stem from the ease with which they can be synthesized, their versatility and also due to their wide ranging complexing ability [1]. The survey of literature reveals that the study of this diverse ligand system is linked with many of the key advances made in inorganic chemistry and has played a seminal role in the development of modern co-ordination chemistry [2], inorganic biochemistry [3], catalysis [4], optical materials [5], etc. A large number of Schiff bases and their metal complexes have been studied because of their ability to reversibly bind oxygen [6] and their use in oxygenation and oxidation reaction of organic compounds [7], redox systems in biological processes [8], aldol reactions [9], textile industries [10], radio pharmaceuticals [11], oxidation of DNA [12] and also in host of other important spheres.

Studies involving complexes of 3d-transition elements with Schiff base ligand are of current interest not only due to their relevance to biological systems [13] but also because many of them exhibit unusual magnetic properties [14], novel structural features [15], antibacterial [16] and catalytic properties [17]. In view of importance of Cr^{III}, Mn^{II}, Co^{II} and Ni^{II} complexes, we have isolated and characterized some new complexes from these metals of a potential multidentate Schiff base derived for 4-aminoantipyrine and 2,4-dihydroxyacetophenone.

EXPERIMENTAL

4-Aminoantipyrine and 2,4-dihydroxyacetophenone were procured from Sigma-Aldrich, USA and used as supplied. The other chemicals and solvents were commercially available (E. Merck). Solvent were used as received.

Synthesis of ligand: The Schiff base ligand (AAPDHA) was synthesized from 4-aminoantipyrine and 2,4-dihydroxyacetophenone by refluxing their equimolar solutions in methanol on a water bath for about 1-2 h on cooling. The crystals were filtered, washed with methanol and recrystallized with hot methanol and dried *in vacuo* at ambient temperature (yield: 85%) (Scheme-I).



Scheme-I

Synthesis of metal complexes: The metal complexes were synthesized by refluxing an ethanolic solution of Schiff base ligand (30 mL, 1 mmol.) with a solution of corresponding metal salt (50 mL, 2 mmol.) for 10-20 h at 70-85 °C [9]. On cooling overnight at 0 °C, the coloured complex was precipitated out, which was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10} .

RESULTS AND DISCUSSION

All the chelates are deeply coloured and non-hygroscopic solids. They are soluble in methanol, ethanol and partially soluble in water and insoluble in ether and benzene. The micro-analytical data of complexes with their physical properties (Table-1) showed that all the complexes are mononuclear with general formula: $[M^I LX]$ and $[M^{II} LX]$, where L = AAPDHA and X = NO_3^- , $M^I = Cr^{II}$, Mn^{II} , Co^{II} and $M^{II} = Ni^{II}$. The molar conductance values of the complexes were measured for 10^{-3} M in nitrobenzene, acetonitrile and methanol, which adequately confirmed the non-electrolytic nature of metal complexes [18].

Table-1 Microanalytical data of complexes with their Physical Properties.

| S. No. | Complex | Colour | m.p. (°C) | Molar conductance ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) | Microanalytical Calculated (found) % | | | | |
|--------|------------------------|--------------|-----------|---|--------------------------------------|------------------|----------------|-----------------|----------------|
| | | | | | Cr | C | H | N | O |
| 1 | $C_{19}H_{19}N_5O_9Cr$ | Violet | 285 | 9 | 11.3 (11.1) | 44.44 (44.4) | 3.703 (3.6) | 13.6 (13.3) | 28.7 (28.3) |
| 2 | $C_{23}H_{25}N_3O_7Cr$ | Violet | > 295 | 15 | 12.7 (12.4) | 67.8 (67.5) | 6.1 (5.9) | 10.3 (10.1) | 27.5 (27.1) |
| 3 | $C_{19}H_{19}N_5O_9Mn$ | White | > 300 | 15 | 17.4 (17.0) | 72.1 (71.9) | 6.01 (6.0) | 22.1 (22.0) | 45.5 (45.0) |
| 4 | $C_{19}H_{19}N_5O_9Co$ | Pink | > 300 | 20 | 18.4 (18.1) | 71.2 (71.0) | 5.9 (5.4) | 2.1 (2.0) | 45.0 (45.0) |
| 5 | $C_{23}H_{25}N_3O_7Mn$ | White | > 300 | 3 | 12.3 (12.1) | 60.74 (60.70) | 5.27 (5.23) | 9.2 (8.9) | 24.6 (24.2) |
| 6 | $C_{23}H_{25}N_3O_7Co$ | Pink | > 292 | 13 | 14.2 (14.0) | 66.6 (66.1) | 6.04 (6.0) | 10.7 (10.3) | 24.6 (24.2) |
| 7 | $C_{19}H_{19}N_4O_6Ni$ | Greyish blue | > 300 | 26 | 11.6 (11.2) | 44.8 (44.3) | 3.7 (3.4) | 11.02 (11.0) | 18.8 (18.3) |
| 8 | $C_{21}H_{22}N_3O_5Ni$ | Greyish blue | > 300 | 28 | 12.9 (12.4) | 55.6 (55.3) | 4.8 (4.4) | 9.2 (9.0) | 17.5 (17.1) |

Table-2 Spectral data of the Schiff base ligand (AAPDHA) and its metal Complexes

| Ligand/Complexes | | Infrared assignments (cm ⁻¹) | | | | |
|------------------|---|--|--------------------------|--------------------------|--------------------------|--------------------------|
| | | $\nu(\text{OH})$ | $\nu(\text{C}=\text{O})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{M}-\text{N})$ | $\nu(\text{M}-\text{O})$ |
| AAPDHA | | 2974 | 1685 | 1620 | - | - |
| 1. | [Cr ^{III} (AAPHA)(NO ₃) ₂] | 2965 | 1656 | 1605 | 490 | 660 |
| 2. | [Cr ^{III} (AAPHA)(OAc) ₂] | 2963 | 1657 | 1603 | 492 | 662 |
| 3. | [Mn ^{II} (AAPHA)(NO ₃) ₂] | 2967 | 1659 | 1609 | 497 | 665 |
| 4. | [Co ^{II} (AAPHA)(NO ₃) ₂] | 2968 | 1665 | 1615 | 499 | 669 |
| 5. | [Mn ^{II} (AAPHA)(OAc) ₂] | 2966 | 1660 | 1610 | 498 | 666 |
| 6. | [Co ^{II} (AAPHA)(OAc) ₂] | 2969 | 1660 | 1618 | 900 | 470 |
| 7. | [Ni ^{II} (AAPHA)(NO ₃) ₂] | 2970 | 1669 | 1624 | 502 | 673 |
| 8. | [Ni ^{II} (AAPHA)(OAc) ₂] | 2972 | 1671 | 1626 | 505 | 676 |

Infrared spectra: The selected vibrational bands and assignments of the Schiff base ligand and their metal complexes are listed in Table-2. The infrared spectrum of the free ligand exhibited a broad band of medium intensity at $\sim 2974 \text{ cm}^{-1}$, assignable to hydrogen bonded-OH group. This band disappears on complexation in all the cases. A broad medium intensity band observed at is $\sim 3400 \text{ cm}^{-1}$ confirmed the presence of free -OH groups and their non-participation in coordination with the metal ion. The $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ azomethine observed at 1685 and 1630 cm^{-1} , respectively, in the spectrum of Schiff base ligand show a downward Schiff (~ 1656 and 1605 cm^{-1}) in all the complexes [18]. These suggest the participation of the pyrazol-carbonyl and azomethine groups in coordination and the ligand act as a neutral bidentate coordinating through the $>\text{C}=\text{O}$ and $>\text{C}=\text{N}$ groups, only. Moreover, in the IR spectra of complexes, the new bands appear in the range 505-490 and 676-660 cm^{-1} which may be assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ stretching vibrations [10]. The nitrate complexes show IR bands at 1495-1440 (ν_5), 1325-1270 (ν_1) and 1088-1098 (ν_2) cm^{-1} and the value of $\Delta(\nu_5 - \nu_1)$ i.e. 23 cm^{-1} indicates the bidentate coordination of NO₃⁻ ion [15]. The acetate complexes show the IR bands in the region of 1485-1395 and 1380-1315 cm^{-1} due to $\nu_{\text{asym}}(\text{OAc})$ and $\nu_{\text{sym}}(\text{OAc})$ stretching vibrations. Moreover, the difference in the $\Delta\nu$ value i.e. 51 cm^{-1} suggests the bidentate coordination of the acetate anion [16].

Electronic spectra:- The electronic spectra of the synthesized metal complexes were recorded in DMSO or DMF solution. The electronic spectra of Cr^{III} complexes display the transitions the range 15870-15940 and 22465-26935 cm^{-1} , which may be assigned to the ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1) and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ (ν_2) spin allowed $d-d$ transitions. These transitions revealed that Cr^{III} ion is in octahedral environment [18]. The electronic spectra of the complexes also display the third transition in the range 35710-36781 cm^{-1} due to charge transfer band.

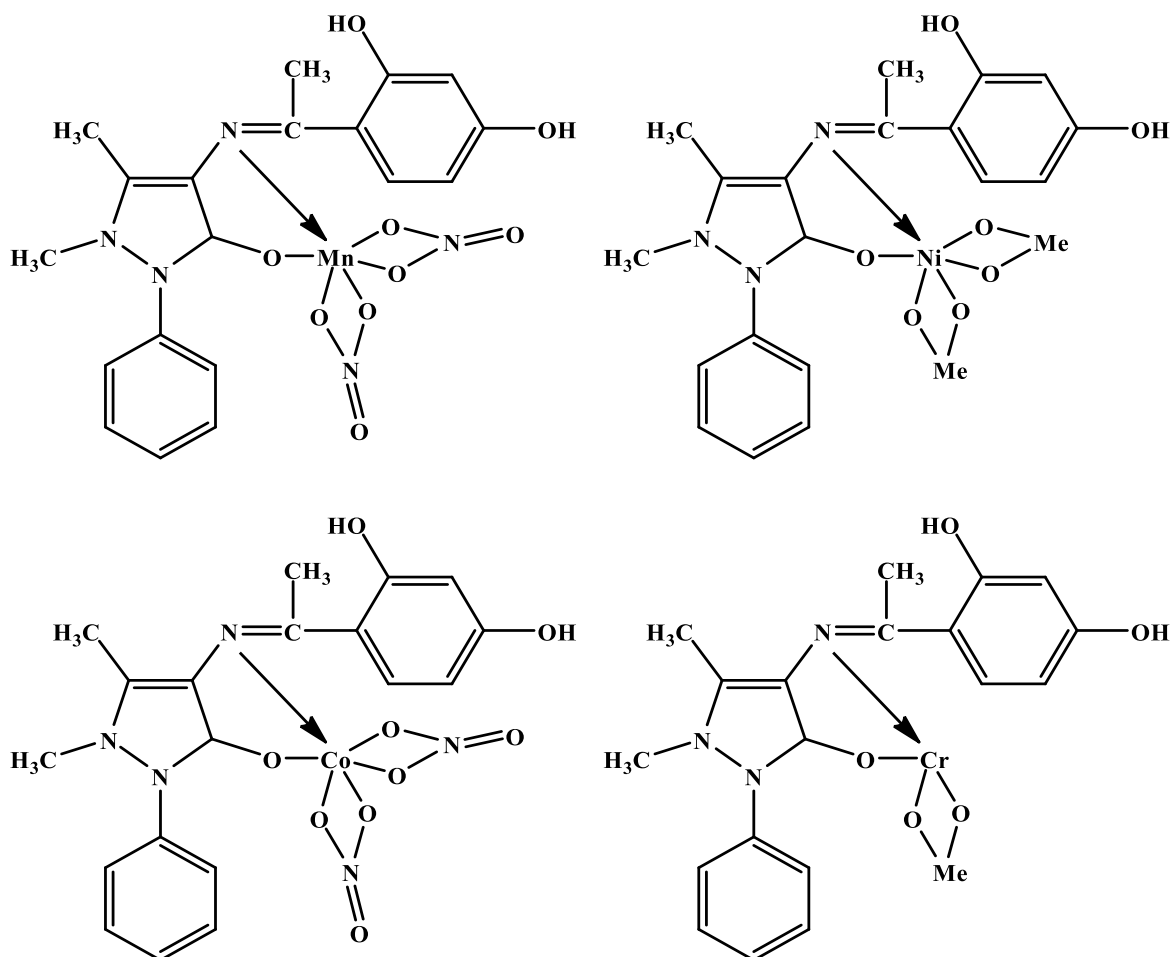
The electronic spectra of Mn^{II} complexes display the absorption bands in the range 18579-18621, 22465-24290, 27391-28161 and 36492 cm^{-1} . These transitions may be assigned to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(4g)$, ${}^6\text{A}_{1g} \rightarrow 4\text{E}_g$, ${}^4\text{A}_{1g}(4g)$, ${}^6\text{A}_{1g} \rightarrow 4\text{E}_g(4D)$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$, respectively. The band at 45451 cm^{-1} corresponds to the charge transfer band and these transitions suggest the octahedral geometry for the complexes [17].

The electronic spectra of Co^{II} complexes display the absorption bands in the region 10425-10701, 18619-18674 and 22118-22317 cm^{-1} . These transitions may be assigned to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1), ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ (ν_2) and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) transitions, respectively. These transitions correspond to the tetragonal geometry around the Co^{II} metal center [16]. The absorption bands in the electronic Spectra of the complexes are also present in the region of 27318-38015- cm^{-1} , which may be assigned to the intra-ligand and charge transfer bands.

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The absorption spectra of Ni^{II} complexes display *d-d* transition bands in the range 13120-15475, 18581-18860 and 24151-27244 cm⁻¹. The lowest energy transition corresponds to the transition ¹A_{1g} → ¹A_{2g} (d_{xy} → d_{x²-y²}) (ν₁), which suggests that the energy levels order is d_{z²} < d_{xy} [19]. The other transitions corresponds to ¹A_{1g} → ¹B_{1g} (d_{z²} → d_{x²-y²}) (ν₂) and ¹A_{1g} → ¹E_g (d_{xy}, d_{yz} → d_{x²-y²}) (ν₃), respectively.

These transitions reveal that the nickel complexes possess square planar geometry and D_{4h} symmetry [18]. The complexes display ν₁ band at higher energy in comparison to that of the octahedral complexes. This is because of the reason that the crystal field energy for square planar complexes is large and the energy separation between d_{x²-y²} orbital and the next lowest orbital is higher as compared to the octahedral complexes [18]. Based on these spectral data, the tentative structures of the metal complexes are assigned as follows:



Antimicrobial studies: The antibacterial activities of the Schiff base ligand (AARDHA) and its metal complexes were tested against *Enterobacter aerogenes* ATCC 12666 and *E. coli* ATCC 25922 by disc diffusion method [19] at concentration of 10 µg per disc using penicillin as positive control and chloroform as negative control. The results showed that the Schiff base ligand did not possess any antibacterial property but the complexes showed the antibacterial activity. The Schiff base ligand and its metal complexes were screened for their possible antifungal activity against *Aspergillus flavus* ATCC 1027 and *Penicillium* Sp. ATCC 10115 by disc diffusion method at a concentration of 10 µg per disc using gresiofulvin as positive control and chloroform as negative control. The results showed that the Schiff base ligand did not show any antifungal activity, however, complexes of Mn^{II} showed moderate antifungal activity.

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