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Synthesis and Spectral Studies of Some Metal Complexes of Some Phenylhydrazones

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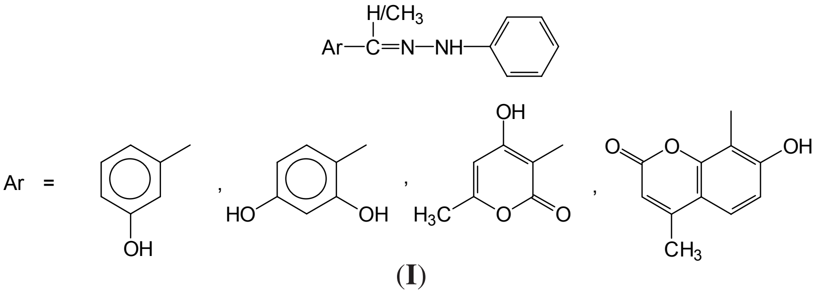
Fe(III), Ni(II), Cu(II), Ru(III) and Pd(II) complexes of phenylhydrazones derived from 3-hydroxy benzaldehyde, resorcealdehyde, dehydro acetic acid and 7-hydroxy-4-methyl-8-acetyl coumarin have been synthesized and characterized by physico-chemical data. All the ligands behave as mononegative, bidentate ones. The geometry and the bonding characteristics of the complexes have been deduced from relevant data.

Key Words: Synthesis, Metal complexes, Phenylhydrazones.

INTRODUCTION

Hydrazones, simple as well as substituted ones are potential organic ligands for metals usually from the transition groups forming chelates. These compounds constitute an important class owing to their coordinating capability, analytical and industrial potentiality and biological activity[1,2]. The literature survey reveals that phenylhydrazones, of all the substituted hydrazones have been little explored as chelating agents, despite their promising nature. Phenylhydrazones find use mainly in qualitative and gravimetric analyses, as indicators of high alkalinity and in spectrophotometric and catalytic procedure[3-5]. With an objective of exploring the applicability of this class of hydrazones, we report herein, the synthesis and spectral characterization of Fe(III), Ni(II), Cu(II), Ru(III) and Pd(II) complexes of 3-hydroxybenzaldehyde phenylhydrazone (HBPH), resorcealdehyde phenylhydrazone (RAPH), dehydroacetic acid phenylhydrazone (DAPH) and 7-hydroxy-4-methyl-8-acetyl-coumarin phenylhydrazone (HCPH) (**I**).



(**I**)

EXPERIMENTAL

All the chemicals used were of AR or BDH grade. The ligands HBPH, RAPH, DAPH and HCPH were prepared by refluxing equimolar solutions of phenylhydrazine hydrochloride in sodium acetate-water and the respective aldehydes in methanol for 2-3 h. The solid that separated on cooling was filtered, washed with cold methanol and recrystallized from dry methanol. The colour, yield %, m.p (ºC) and elemental analysis (%) of HBPH, RAPH, DAPH and HCPH are respectively brown, 70, 148 [Found (%) C, 73.44; H, 5.65; N, 13.26; $C_{13}H_{12}N_2O$ requires (%) C, 73.55; H, 5.71; N, 13.20]; pale brown, 70, 159-161 [Found (%) C, 68.28; H, 5.25; N, 12.20; $C_{13}H_{12}N_2O_2$ requires (%) C, 68.40; H, 5.40; N, 12.28; $C_{14}H_{14}N_2O_3$ requires (%) C, 65.09; H, 5.47; N, 10.85] and pale yellow, 85, 120 [Found (%) C, 69.92; H, 5.20; N, 8.97; $C_{18}H_{16}N_2O_3$ requires (%) C, 70.10; H, 5.24; N, 9.09].

The Fe(III), Ru(III) and Pd(II) complexes with all the ligands were prepared using respective metal chlorides and Ni(II) and Cu(II) complexes using metal acetates. In the preparation of the metal complexes the metal and the ligand were combined in 1:3 ratio in the case of Fe(III) and Ru(III) complexes and 1:2 ratio in the case of Ni(II), Cu(II) and Pd(II) complexes using required quantities of methanol so as to effect the solubility of the metal salts and the ligands. The contents were refluxed on a hot water bath for 2-3 h and the solid that separated out was filtered, washed with water, hot methanol and ether and was vacuum dried over fused $CaCl_2$.

The elemental analyses (C, H, N) for the ligands and their metal complexes were obtained from RSIC, CDRI, Lucknow. A Digisun digital conductivity meter, DI 909 model was used for measuring the conductance of the metal complexes in DMF at 10^{-3} M concentration. Gouy balance calibrated with $Hg[Co(NSC)_4]$ was used to measure the magnetic susceptibility of the metal complexes in solid state at room temperature. Diamagnetic corrections were calculated from Pascal's constants[6]. The IR spectra of the ligands and the metal complexes in KBr were recorded in the range 4000-450 cm^{-1} employing Bruker IFS-66V FTIR spectrophotometer. The electronic spectra of the metal complexes in DMF were recorded on Jasco 7800 Elico SL-159 and Shimadzu UV-160A UV-Vis spectrophotometers. The Varian E-112 EPR spectrophotometer operating in the frequency range 8.8-9.6 GHz was employing in recording the ESR spectra of Cu(II) and Ru(III) complexes in DMF solution at liquid nitrogen temperature. The chloride content in Fe(III), Ru(III) and Pd(II) complexes and the metal content in Fe(III), Ni(II), Cu(II) and Pd(II) complexes, after decomposition, were determined by standard procedures-chloride by Volhard's method, iron, after reduction, by dichrometry, copper by iodometry and nickel and palladium by gravimetry[7].

RESULTS AND DISCUSSION

All the metal complexes (Table-1) are coloured, stable at room temperature and are non-hygroscopic. Upon heating, they decompose without melting. The complexes are insoluble in water, slightly soluble in hot methanol and fairly soluble in DMF. All the metal complexes are shown in DMF to be non-electrolytic with only residual conductance values (11-15 Ω^{-1} cm^2 mol^{-1}). The magnetic moment data indicate that Fe(III), Cu(II) and Ru(III) complexes of all the ligands are paramagnetic to the extent of five, one and one unpaired electrons respectively and that the Ni(II) and Pd(II) complexes are diamagnetic.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE METAL COMPLEXES

Metal complex	Colour	Metal % Found (calcd.)	μ_{eff} (BM)
$Fe(C_{13}H_{11}N_2O)_3$	Reddish brown	7.90 (8.09)	5.70
$Ni(C_{13}H_{11}N_2O)_2$	Greenish yellow	12.03 (12.12)	–
$Cu(C_{13}H_{11}N_2O)_2$	Pale yellow	12.89 (13.07)	1.83
$Ru(C_{13}H_{11}N_2O)_3$	Brown	–	1.90
$Pd(C_{13}H_{11}N_2O)_2$	Green	19.98 (20.11)	–
$Fe(C_{13}H_{11}N_2O_2)_3$	Light brown	7.36 (7.57)	5.76
$Ni(C_{13}H_{11}N_2O_2)_2$	Yellow	11.16 (11.43)	–
$Cu(C_{13}H_{11}N_2O_2)_2$	Yellowish green	12.00 (12.26)	1.81
$Ru(C_{13}H_{11}N_2O_2)_3$	Brown	–	1.90
$Pd(C_{13}H_{11}N_2O_2)_2$	Pale green	18.72 (18.96)	–
$Fe(C_{14}H_{13}N_2O_3)_3$	Reddish brown	6.62 (6.75)	5.72
$Ni(C_{14}H_{13}N_2O_3)_2$	Pale brown	10.05 (10.24)	–
$Cu(C_{14}H_{13}N_2O_3)_2$	Pale green	10.76 (10.99)	1.84
$Ru(C_{14}H_{13}N_2O_3)_3$	Brown	–	1.87
$Pd(C_{14}H_{13}N_2O_3)_2$	Green	17.02 (17.13)	–
$Fe(C_{18}H_{15}N_2O_3)_3$	Brown	5.45 (5.71)	5.69
$Ni(C_{18}H_{15}N_2O_3)_2$	Pale yellow	8.52 (8.71)	–
$Cu(C_{18}H_{15}N_2O_3)_2$	Pale brown	9.12 (9.36)	1.83
$Ru(C_{18}H_{15}N_2O_3)_3$	Dark brown	–	1.91
$Pd(C_{18}H_{15}N_2O_3)_2$	Brown	14.55 (14.75)	–

All the metal complexes gave satisfactory C, H, N analyses.

All the ligands show small or medium intensity band around 3324-3133 cm^{-1} which has been assigned to NH stretching[8]. This band does not undergo lower shift in the complexes ruling out the possibility of involvement of nitrogen of this group in co-ordination. A strong band that appears around 1600 cm^{-1} in all the ligands due to ν(C=N) has been found shifted to lower frequency about 20-40 cm^{-1} in the complexes suggesting that the nitrogen of this group is involved in coordination[9]. The ligands HBPH, RAPH, DAPH and HCPH reveal a small band in the region 3528-3352 cm^{-1} that has been ascribed to ν(O–H). This band disappears in the spectra of complexes indicating that the deprotonation of the group has taken place. A strong band around 1250 cm^{-1} in these ligands assignable to ν(C–O) is found to have undergone a positive shift by about 20 cm^{-1} in their complexes. This positive shift indicates coordination of the deprotonated hydroxy group[10]. Thus, the ligands function as mononegative bidentate ones, coordinating through phenolic oxygen and azomethine nitrogen.

The electronic spectral frequencies observed for the complexes along with ligand field parameters for the Ru(III) complexes are given in Table-2. These frequencies may be assigned, in the increasing order, to the transitions as detailed below[11-14].

Fe(III) complexes : $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4E_g(G)$,
Ni(II) complexes : $^1A_{1g}(D) \rightarrow {}^1E_g(G)$ and charge transfer
Cu(II) complexes : $^2B_{1g} \rightarrow {}^2B_{2g}$
Ru(III) complexes : $^2T_{2g} \rightarrow {}^4T_{1g}$, $^2T_{2g} \rightarrow {}^4T_{2g}$ and $^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$
Pd(II) complexes : $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$

TABLE-2
ELECTRONIC SPECTRAL DATA OF THE METAL COMPLEXES

Metal complex	Frequency (cm^{-1})			B (cm^{-1})	C (cm^{-1})	10Dq (cm^{-1})	β
Fe-HBPH	15873	22883	28736	–	–	–	–
Ni-HBPH	24425	26212	–	–	–	–	–
Cu-HBPH	15950	–	–	–	–	–	–
Ru-HBPH	14706	18519	25000	477	1908	24723	0.76
Pd-HBPH	13158	17331	22026	–	–	–	–
Fe-RAPH	15429	21945	29034	–	–	–	–
Ni-RAPH	24609	26723	–	–	–	–	–
Cu-RAPH	15890	–	–	–	–	–	–
Ru-RAPH	14724	18530	24948	476	1904	24720	0.76
Pd-RAPH	13036	17258	22000	–	–	–	–
Fe-DAPH	15630	22818	28896	–	–	–	–
Ni-DAPH	24446	26800	–	–	–	–	–
Cu-DAPH	16010	–	–	–	–	–	–
Ru-DAPH	14802	18564	24893	470	1880	24672	0.75
Pd-DAPH	13345	17024	22242	–	–	–	–
Fe-HCPH	15764	22859	28618	–	–	–	–
Ni-HCPH	24510	26316	–	–	–	–	–
Cu-HCPH	16025	–	–	–	–	–	–
Ru-HCPH	14784	18545	24900	470	1880	24654	0.75
Pd-HCPH	13320	17010	22190	–	–	–	–

Based on these transitions and the other data observed, high-spin octahedral geometry for the Fe(III) complexes, low spin octahedral geometry for the Ru(III) complexes and square planar geometry for the Cu(II), Ni(II) and Pd(II) complexes have been proposed.

The ligand field parameters B, C, 10DQ and β for the Ru(III) complexes have been calculated using the transitions[15].

$$^2T_{2g} \rightarrow 4T_{1g} \quad = \quad 10\,DQ - 5B - 4C$$

$$^2T_{2g} \rightarrow 4T_{2g} \quad = \quad 10\,DQ + 3B - 4C$$

and assuming that C/B = 4.

The Racah interelectron repulsion parameter B observed for the complexes is less than that for the Ru(III) ion (B' = 630 cm^{-1})[16]. 10 DQ value is quite high and further, the nephelauxetic parameter $\beta = B/B'$ is less than one. These observations suggest that the metal-ligand bond in the present complexes is covalent in nature[17].

The ESR spectral data for the Cu(II) and Ru(III) complexes are incorporated in Table-3.

TABLE-3
ESR SPECTRAL DATA OF Cu(II) AND Ru(III) COMPLEXES

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel} \times 10^4$ (cm^{-1})	$A_{\perp} \times 10^4$ (cm^{-1})	$A_{ave} \times 10^4$ (cm^{-1})	α^2	β^2
Cu-HBPH	2.28	2.05	2.13	1061	633	776	0.793	0.843
Cu-RAPH	2.28	2.04	2.12	949	558	688	0.770	0.865
Cu-DAPH	2.27	2.06	2.13	1256	279	605	0.793	0.816
Cu-HCPH	2.30	2.06	2.14	1237	465	726	0.816	0.883
Ru-HBPH	1.95	2.22	2.13	–	–	–	–	–
Ru-RAPH	1.98	2.31	2.20	–	–	–	–	–
Ru-DAPH	1.89	2.16	2.07	–	–	–	–	–
Ru-HCPH	1.93	2.20	2.11	–	–	–	–	–

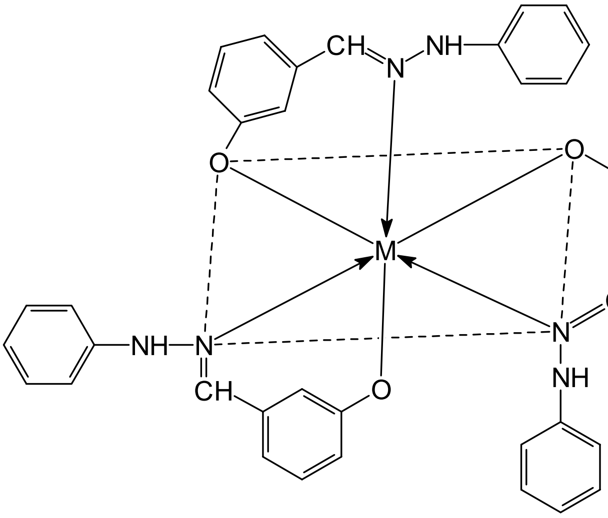
$G_{ave} = 1/3\,(g_{\parallel} + 2\,g_{\perp})$; $A_{ave} = 1/3\,(A_{\parallel} + 2\,A_{\perp})$.

The spectra of Cu(II) complexes are anisotropic in nature in that each of them has two peak envelopes, one of small intensity towards low field and the other of large intensity towards high field, partially resolved due to hyperfine interaction with copper nucleus. The $g_{\parallel}$ and $g_{\perp}$ components have been calculated respectively from the low intensity and high intensity envelopes. The values obtained for the complexes are $g_{\parallel} > g_{\perp} > 2$ indicating that the unpaired electron lies in $d_{x^2-y^2}$ orbital typical of an elongated octahedral case[18-20]. Further, the values of α^2, the in-plane σ-bonding parameter and β^2, the in-plane π-bonding parameter evaluated for the complexes are suggestive of moderate covalency associated with them[21,22].

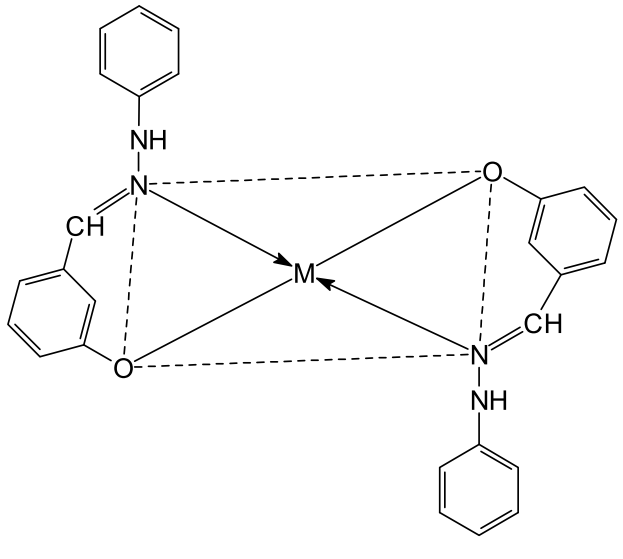
The ESR spectra of the Ru(III) complexes show a six line pattern due to hyperfine interaction of the unpaired electron with the nuclear spin

$I_{Ru} = 5/2$. The shape of the spectra observed may be rationalized in terms of the low-spin nature of the complexes. The t^5_{2g} configuration of a Ru(III) complex constitutes a positive hole in t_{2g} orbital set and so $g_\perp > g_\parallel$ is expected[20,23]. The g values obtained for the complexes are in the range 2.07-2.20 reported for the low-spin Ru(III) octahedral complexes[24].

Based on the foregoing discussion, tentative structures for the representative metal complexes of HBPH may be proposed as follows:



M = Fe, Ru



M = Cu, Ni, Pd

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