Synthesis and characterization of iron(III), cobalt(II), nickel(II), copper(II), ruthenium(II, III), rhodium(III) and palladium(II) complexes with N-(2-carboxyphenyl)- and 2-amino-N-(2-carboxyphenyl)-benzamides

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N-(2-Carboxyphenyl)- and 2-amino-N-(2-carboxyphenyl)-benzamide complexes of Fe(III), Co(II), Ni(II), Cu(II), Ru(II), Ru(III), Rh(III) and Pd(II) have been prepared and characterized by physicochemical, thermal, spectral and magnetic methods. The coordination sites of ligands are confirmed by the absorptions in the IR and NMR spectra of diamagnetic complexes. Further, the geometry of the complexes has been established by electronic spectra, ESR studies of paramagnetic Ru(III) and Cu(II) complexes and Mössbauer spectra of Fe(III) complexes. N-(2-Carboxyphenyl)-benzamide is found to be a uninegative bidentate ligand coordinating through carboxylic oxygen and amide nitrogen while 2-amino-N-(carboxyphenyl)-benzamide has been a tridentate ligand in all its complexes except in the case of Ru(II), in which it coordinates through amine and amide nitrogen atoms only.

Preparation of complexes

General method

The metal salt (2 mmol) (chloride in the case of Fe(III), Ru(III), Rh(III), Pd(II); acetate in the case of Co(II), Ni(II), Cu(II) or [Ru(DMSO)₄]Cl₂) was dissolved in water. To this, 4 mmol of ligand CPBH/ACPBH in methanol (30 ml) was added slowly, with constant stirring. The mixture was refluxed for 1-2 h. The Co(II), Ni(II), Cu(II), Ru(II), Ru(III), Rh(III), Pd(II) and Cu(II) complexes separated out were filtered and washed thoroughly with acetone and ether and then dried over fused CaCl₂. In the case of the complexes of Fe(III), Ru(II) and Ru(III), the reaction mixture was concentrated to 10 ml under reduced pressure and cooled at -20°C overnight. The separated solids were filtered, washed and dried, yield, 60-85%.

The elemental analyses using a Perkin-Elmer CHN analyser 2400 and ¹H NMR spectra on Brucker 8-SI spectrometer were obtained from Institut für Anorganische und Analytische Chemie der Technische Universität Berlin, Germany. The electronic spectra were recorded on Schimadzu MPS-5000 spectrophotometer. The conductance measurements were made using a DigiSun digital conductivity meter, DI-909. The infrared spectra (4000-200 cm⁻¹) were recorded on a Perkin-Elmer 283 spectrometer in Nujol mulls between CsI plates. The magnetic susceptibility measurements were done by the Guoy’s method using a vibrating sample magnetometer. The ESR spectra at room temperature and at liquid nitrogen temperature were recorded on a JEOL-JES-PE-3X model spectrometer and Varian ESR spectrometer re-
spectively. The DTA curves were recorded on Leeds and Northrup DTA Unit (USA) with Pt and Pt+10%Rh thermocouples. The TG-DSC thermograms were recorded in the temperature range 35-650°C on Mettler-TA-2000C model. The Mössbauer spectra were recorded on a Elsint spectrometer working in constant acceleration mode in conjunction with a multichannel analyser using 512 channels. The Mössbauer spectrometer was calibrated using sodium nitroprusside and iron foil for quadrupole and magnetically split spectra, respectively.

The metal and chloride contents of the complexes were determined by standard volumetric or gravimetric methods\textsuperscript{11}.

**Results and Discussion**

All the complexes are non-hygroscopic and

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Complexes</th>
<th>Found (Calc.) %</th>
<th>Ω\textsubscript{M} (mho cm\textsuperscript{2} mol\textsuperscript{-1})</th>
<th>(\mu)\textsubscript{eff} B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Fe(CPB)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}]Cl</td>
<td>55.02 3.98 4.72 5.62 9.05</td>
<td>36.0</td>
<td>6.00</td>
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<tr>
<td>2</td>
<td>[Fe(ACPB)\textsubscript{2}]Cl</td>
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<td>3</td>
<td>Ru(CPB)\textsubscript{2}(DMSO)\textsubscript{2}]</td>
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<td>8.5</td>
<td>Dia</td>
</tr>
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<td>4</td>
<td>[Ru(ACPBH)(DMSO)\textsubscript{2}]Cl\textsubscript{2}</td>
<td>32.08 4.38 3.38 9.10 —</td>
<td>57.5</td>
<td>Dia</td>
</tr>
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<td>5</td>
<td>[Ru(ACPB)(DMSO)\textsubscript{2}]Cl</td>
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<td>Dia</td>
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<td>1.82</td>
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<td>1.65</td>
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<td>9</td>
<td>Co(ACPB)\textsubscript{2}2H\textsubscript{2}O</td>
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<td>[Rh(ACPB)\textsubscript{2}]Cl</td>
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<td>Ni(CPB)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}]</td>
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<td>3.10</td>
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<tr>
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</tr>
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<td>15</td>
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<td>Dia</td>
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<tr>
<td>16</td>
<td>Cu(CPB)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}]</td>
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<td>[Cu(ACPB)(OAc)\textsubscript{1.5}H\textsubscript{2}O</td>
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<td>1.87</td>
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*Calculated values
stable at room temperature. The Co(II), Ni(II) and Cu(II) complexes of both ligands are insoluble in common organic solvents but are soluble in DMSO and DMF, while other complexes are soluble in methanol, ethanol, acetonitrile etc. The characterization data of the complexes are presented in Table 1.

The thermograms of complexes 1, 8, 12 and 16 show initial mass loss in the temperature range 150-200°C, corresponding to the loss of two water molecules. This loss indicates that the water molecules in these complexes are coordinated. This is further evidenced by the endothermic peaks in the range 150-200°C in the DSC curves. All these complexes show multistage decomposition with the gradual loss of water molecules and one and two ligand molecules. The Co(II)-ACPB complex (9) and Cu(II)-ACPB complex (17) show initial weight loss from 60-120°C and corresponding endothermic peaks in the DSC curves. The loss in weight in this range has been calculated and was found to correspond to 2 and 1.5 water molecules respectively. The loss of water molecules in this low temperature region indicate that they are present as lattice held water. The other complexes do not show any endothermic peaks up to 230°C, but a gradual loss of weight is observed in two or three stages, with corresponding exothermic peaks in the DSC curves. The final residue corresponds to the metallic oxide.

The IR spectrum of CPBH and ACPBH show the following characteristic absorptions (cm
-1)

CPBH: 3440 ν(N-H), 1670 & 1320 ν(C=O) [amide-I], 1520 ν(C-N) + δ(N-H)[amide-II]

ACPBH: 3490, 3380, 3160 ν(N-H) [amine + amide], 1680 ν(C=O), 1640 ν(C=O) [amide-II], 1580 ν(C-N) + δ(N-H)[amide-II]

The IR spectra of the complexes (except that of 4) do not show the characteristic stretching frequency of carboxylic group at 1670/1680 cm
-1 and at 1300 cm
-1 (ref. 13). The disappearance of the absorptions indicate the complexation through COO
- group which is further supported by two new absorptions in the range 1500-1590 cm
-1 and 1350-1420 cm
-1, which may be assigned to ν(CO) and ν(COO) modes of the coordinated carboxylate (monodentate) anion. These modes are at comparatively lower frequency than those observed in the case of sodium salts of the ligands. The IR spectrum of complex 4 shows the stretching modes of -COOH group in the complex. This was further confirmed by the presence of two Cl
- ions outside the coordination sphere (molar conductance, 57.5 ohm
-1 cm
2 mol
-1 and percentage of chlorine). The elemental analysis and physical data indicate that ACPBH in this complex is a bidentate neutral ligand. Further, the complexes 5, 6 and 10 were prepared using sodium salts of ligand anions, CPB
- and ACPB
- . The complex 5 analysed for [Ru(ACPB)(DMSO)\textsubscript{3}]Cl and the molar conductance was found to be 30.2 ohm
-1 cm
2 mol
-1 indicating it to be 1:1 electrolyte and that ACPB acts as a tridentate ligand. The amide stretching frequencies in the IR spectra of complexes were found to have shifted by 100-120 cm
-1 to lower frequency side indicating that the amide nitrogen is coordinated to the metal ions. The participation of -NH\textsubscript{2} group of ACPBH in coordination was evidenced by the low frequency shift (60-90 cm
-1) of ν(N-H) in the spectra of complexes compared to its position in the uncoordinated compound. The ν(C=O) [amide-I] frequency found in the IR spectra of CPBH and ACPBH respectively show no considerable shift in the spectra of complexes. This rules out the involvement of amide > C=O group in coordination.

The IR spectra of complexes 1, 8, 12 and 16 show absorption bands in the region 3200-3500 cm
-1, indicating the presence of water molecules. An additional band at 840 cm
-1 suggests that water molecules are coordinated to metal ions. The spectra of complexes 9 and 17 show the corresponding frequencies for lattice held water. The spectra of all the complexes show two absorptions in the far infrared region 450-510 cm
-1 and 320-410 cm
-1, which are assignable to ν(M-N) and ν(M-O) respectively. The far IR spectra of complexes 3, 4 and 5 show another absorption at 320 and 310 cm
-1 respectively which may be assigned to ν(M-S). The absorption band at 310 cm
-1 in the spectrum of complex 12 can be assigned to ν(Pd-CI). The magnetic moment values of the complexes studied are presented in Table 1. The Ru(II), Rh(III) and Pd(II) complexes were found to be diamagnetic, while all other complexes are paramagnetic with magnetic moment values close to the spin only values.

The magnetic moment data of Fe(III) complexes indicate that they are high-spin complexes. The d-d transitions in high spin Fe(III) complexes are spin forbidden and hence weak. The high-spin octahedral Fe(III) complexes are expected to show four absorption bands in electronic spectra.
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<table>
<thead>
<tr>
<th>Complex No.</th>
<th>Absorption (cm(^{-1}))</th>
<th>Transition</th>
<th>(10 Dq) (cm(^{-1}))</th>
<th>B</th>
<th>C</th>
<th>(\beta)</th>
<th>LFSE</th>
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<tr>
<td>1</td>
<td>15670, 22780, 28075</td>
<td>(^4T_{1g} \rightarrow ^6A_{1g})</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>16500, 23000, 27930</td>
<td>(^4T_{2g} \rightarrow ^6A_{1g})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>3</td>
<td>18181, 22727 (28404, 31645 (^*))</td>
<td>(^1T_{2g} \rightarrow ^1A_{1g})</td>
<td>20028</td>
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<td>1847</td>
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<td>4</td>
<td>16260, 19230</td>
<td>(^1T_{1g} \rightarrow ^1A_{1g})</td>
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<td>186</td>
<td>1209</td>
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<td>17250, 20410</td>
<td>(^1E_g \rightarrow ^6A_{1g})</td>
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<td>14958, 19580</td>
<td>(^1T_{2g} \rightarrow ^2T_{1g})</td>
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<td>0.78</td>
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<td>275</td>
<td>1100</td>
<td>0.83</td>
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<td>947</td>
<td>-</td>
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<td>(^1T_{2g}(F) \rightarrow ^4T_{1g}(F))</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>11</td>
<td>23640, 32050</td>
<td>(^1T_{2g} \rightarrow ^1A_{1g})</td>
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<td>-</td>
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<td>9980, 16800, 26040</td>
<td>(^1T_{2g} \rightarrow ^3A_{2g})</td>
<td>998</td>
<td>709</td>
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<td>658</td>
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<td>-</td>
<td>-</td>
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<td>15</td>
<td>24090, (35714 (^*))</td>
<td>(^1E_g \rightarrow ^1A_{1g})</td>
<td>-</td>
<td>-</td>
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<tr>
<td>16</td>
<td>13210</td>
<td>(^1T_{2g} \rightarrow ^2E_g)</td>
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<td>-</td>
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<td>15625, 19280</td>
<td>(^1B_{2g} \rightarrow ^2B_{1g})</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
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</table>

*Charge Transfer Transitions

The absorption bands in the electronic spectra of Co(II) and Rh(III) complexes are characteristic for the octahedral geometry\(^{19,28}\). The ratios of \(\nu_2/\nu_1\), 2.09 for Co(II) complexes and 1.35 for Rh(III) complex, further confirm the octahedral geometry. The \(\beta\) values which are less than 1.0, indicate appreciable covalency of the metal-ligand bond. The three transitions observed in the electronic spectra of Ni(II) complexes indicate the octahedral environment around the metal ion\(^{29}\), which is further supported by the \(\nu_2/\nu_1\) ratio\(^{30}\), 1.68 and 1.74 for complexes, 12 and 13 respectively. Three transitions are expected for square-planar Pd(II) complexes\(^{31}\). But most of the reported Pd(II) complexes do not show all these bands\(^{31}\). The Pd(II) complexes of CPB and ACPB show two and one band respectively (Table 2) along with one charge transfer band. The six coordinate Cu(II) complex (16) is expected to be tetragonal and is confirmed by the characteristic absorption at 13210 cm\(^{-1}\) assignable to \(^2T_{2g} \rightarrow ^2E_g\) transition. The Cu(II) complex (17) with ACPB, a tridentate ligand, has been found to have an acetate group in the coordination sphere. The geometry of this complex may be assigned as distorted square planar from the corresponding to the transitions—

\(\ ^4T_{1g} \rightarrow ^6A_{1g}\),
\(\ ^4T_{2g} \rightarrow ^6A_{1g}\),
\(\ ^4E_g \rightarrow ^6A_{1g}\), and \(\ ^4T_{2g}(D) \rightarrow ^6A_{1g}\) (ref. 23). But, all these four transitions are not generally observed. In the present investigation, the Fe(III) complexes exhibit three absorptions—two of low intensity and one of high intensity. The increase in intensity may be due to borrowing intensity from neighbouring charge transfer band.

The low spin Ru(II) octahedral complexes with \(^1A_{1g}\) as ground term exhibit two allowed transitions in the electronic spectra\(^{24}\). The electronic spectra of low spin Ru(III) complexes are generally complicated with eight transitions from \(^2T_{2g}\) ground state\(^{25}\). The observed absorptions in the spectra of complexes 5 and 7 are assigned as presented in Table 2. The parameters \(10 Dq\), B and C have been evaluated using the electronic transitions\(^{25}\) assuming that C/B = 4 (ref. 26). The considerable decrease in the value of the Racah interelectronic repulsion parameter B, compared to that of free ion value and the higher Dq values suggest that the metal-ligand bonds are covalent\(^{25}\).
In the PMR spectrum of Pd(II)-ACPB, the carboxylic proton resonance signal has disappeared confirming the deprotonation and coordination as understood from earlier studies. Further, the -NHz and -C(O)-NH signals shifted to low field, i.e. to 6.5 and 7.0 ppm respectively. This shows that ACPB acts as a tridentate ligand.

The HNMR spectra of CPBH and ACPBH and diamagnetic Ru(II) and Pd(II) complexes have been recorded in d5-MeOH and d6-DMSO respectively. The well resolved resonance signals have been assigned as follows (δ in ppm)—

**CPBH**: 12.20, (1H) -COOH, 7.2-7.8, (9H) aromatic Hs, 6.7, (1H) -C(O)-NH.

**ACPBH**: 11.8, (1H) -COOH, 7.2-8.9, (8H) aromatic Hs, 6.3, (3H) -NH2 + -C(O)NH.

The HNMR spectrum of Ru(II) complex with ACPBH (4) exhibits a broad signal at 6.82 (2H) and a sharp singlet at 11.78 ppm (1H), which may be assigned to amine and carboxylic protons respectively. The shift in -NH2 signal indicates that amine nitrogen is coordinated to metal ion. Further, the resolution of -COOH signal in the spectrum of the complex and its existence at 11.78 ppm shows that the carboxylic group is not coordinated to the metal ion. The downfield shift of amide proton resonance signal by 1.8 ppm confirms the involvement of amide nitrogen in coordination. In addition to these three (-NHz, -C(O)NH and -COOH) and aromatic protons' resonance signals, a sharp singlet at 3.1 ppm (2H) is also observed. This signal may be attributed to the methyl protons of coordinated DMSO. The complex (5), prepared using the sodium salt of ACPB exhibits the same resonance signals except that of carboxylic proton in its HNMR spectrum. The peak area of the signal corresponding to the methyl protons of coordinated DMSO has been found to be less as compared to that found in the case of complex (4) and corresponds to 18 protons, indicating that ACPB, the tridentate ligand, substituted one more DMSO molecule from the coordination sphere.

The 1HNMR spectra of CPBH and ACPBH and diamagnetic Ru(II) and Pd(II) complexes have been recorded in d5-MeOH and d6-DMSO respectively. The well resolved resonance signals have been assigned as follows (δ in ppm)—

<table>
<thead>
<tr>
<th>g1</th>
<th>g2</th>
<th>g3</th>
<th>gave</th>
<th>Aave</th>
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<td>6</td>
<td>2.413</td>
<td>2.205</td>
<td>2.061</td>
<td>2.216</td>
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<tr>
<td>7 (a)</td>
<td>2.399</td>
<td>2.199</td>
<td>2.030</td>
<td>2.214</td>
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<tr>
<td>(b)</td>
<td>2.357</td>
<td>2.243</td>
<td>2.141</td>
<td>2.102</td>
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<tr>
<td></td>
<td>2.045</td>
<td>1.959</td>
<td>1.869</td>
<td></td>
</tr>
</tbody>
</table>

(\(a\)) At room temperature, (\(b\)) at liquid nitrogen temperature

| g0  | g1  | gave | \(|A_1| \) | \(A_1 \) | \(A_{ave} \) | K\(\beta\) | K\(\perp\) | G | \(\lambda \) |
|-----|-----|------|--------|--------|----------|---------|--------|----|------|
| 13  | 2.210 | 2.050 | 2.103 | 160 | 18 | 65 | 0.40 | 0.51 | 4.20 | 346 |
| 14  | 2.214 | 2.068 | 2.116 | 124 | 19 | 54 | 0.49 | 0.77 | 3.15 | 418 |

The 1HNMR spectra of CPBH and ACPBH and diamagnetic Ru(II) and Pd(II) complexes have been recorded in d5-MeOH and d6-DMSO respectively. The well resolved resonance signals have been assigned as follows (δ in ppm)—

**CPBH**: 12.20, (1H) -COOH, 7.2-7.8, (9H) aromatic Hs, 6.7, (1H) -C(O)-NH.

**ACPBH**: 11.8, (1H) -COOH, 7.2-8.9, (8H) aromatic Hs, 6.3, (3H) -NH2 + -C(O)NH.

The 1HNMR spectra of Ru(II) complex with ACPBH (4) exhibits a broad signal at 6.82 (2H) and a sharp singlet at 11.78 ppm (1H), which may be assigned to amine and carboxylic protons respectively. The shift in -NH2 signal indicates that amine nitrogen is coordinated to metal ion. Further, the resolution of -COOH signal in the spectrum of the complex and its existence at 11.78 ppm shows that the carboxylic group is not coordinated to the metal ion. The downfield shift of amide proton resonance signal by 1.8 ppm confirms the involvement of amide nitrogen in coordination. In addition to these three (-NHz, -C(O)NH and -COOH) and aromatic protons' resonance signals, a sharp singlet at 3.1 ppm (2H) is also observed. This signal may be attributed to the methyl protons of coordinated DMSO. The complex (5), prepared using the sodium salt of ACPB exhibits the same resonance signals except that of carboxylic proton in its HNMR spectrum. The peak area of the signal corresponding to the methyl protons of coordinated DMSO has been found to be less as compared to that found in the case of complex (4) and corresponds to 18 protons, indicating that ACPB, the tridentate ligand, substituted one more DMSO molecule from the coordination sphere.

The 1HNMR spectra of CPBH and ACPBH and diamagnetic Ru(II) and Pd(II) complexes have been recorded in d5-MeOH and d6-DMSO respectively. The well resolved resonance signals have been assigned as follows (δ in ppm)—

**CPBH**: 12.20, (1H) -COOH, 7.2-7.8, (9H) aromatic Hs, 6.7, (1H) -C(O)-NH.

**ACPBH**: 11.8, (1H) -COOH, 7.2-8.9, (8H) aromatic Hs, 6.3, (3H) -NH2 + -C(O)NH.

The 1HNMR spectra of Ru(II) complex with ACPBH (4) exhibits a broad signal at 6.82 (2H) and a sharp singlet at 11.78 ppm (1H), which may be assigned to amine and carboxylic protons respectively. The shift in -NH2 signal indicates that amine nitrogen is coordinated to metal ion. Further, the resolution of -COOH signal in the spectrum of the complex and its existence at 11.78 ppm shows that the carboxylic group is not coordinated to the metal ion. The downfield shift of amide proton resonance signal by 1.8 ppm confirms the involvement of amide nitrogen in coordination. In addition to these three (-NHz, -C(O)NH and -COOH) and aromatic protons' resonance signals, a sharp singlet at 3.1 ppm (2H) is also observed. This signal may be attributed to the methyl protons of coordinated DMSO. The complex (5), prepared using the sodium salt of ACPB exhibits the same resonance signals except that of carboxylic proton in its HNMR spectrum. The peak area of the signal corresponding to the methyl protons of coordinated DMSO has been found to be less as compared to that found in the case of complex (4) and corresponds to 18 protons, indicating that ACPB, the tridentate ligand, substituted one more DMSO molecule from the coordination sphere.

In the PMR spectrum of Pd(II)-ACPB, the carboxylic proton resonance signal has disappeared confirming the deprotonation and coordination as understood from earlier studies. Further, the -NH2 and -C(O)-NH signals shifted to low field, i.e. to 6.8 and 7.0 ppm respectively. This shows that ACPB acts as a tridentate ligand.
The electron spin resonance spectra of Ru(III) and Cu(II) complexes (6, 7, 16 and 17) are recorded at room temperature and liquid nitrogen temperature. The spectral data along with the molecular orbital parameters are given in Table 3.

The room temperature ESR spectra of Ru(III) complex (5) is a simple three line spectrum indicating that the complex is a low spin one. A high spin Ru(III) complex is expected to give a thirty-two line spectrum. This is due to the resolution of spin degeneracy by five unpaired electrons. Each of these five transitions will further split into six lines due to the interaction with the nuclear spin I = 5/2, of 99Ru and 101Ru nuclei. The peak at high field side is more intense than the peaks at low field side. This pattern of the ESR spectrum can be attributed to the normal axial distortion in the complex indicated that one of the chelate rings is less stable than the other and the more stable rings are nearly planar. From this analysis, it may be concluded that ACPB, a tridentate ligand forms one ring coordinating through amine and amide nitrogens (in plane and more stable) and another involving the amide nitrogen and carboxylate oxygen occupying axial positions (less stable), leading to axial distortion.

The LNT ESR spectrum of the same complex shows six line hyperfine splitting with A values around 130 gauss. The six line spectrum is due to strong interactions of nuclear spin, I = 5/2, with the electron spin at low temperature. The lower g values and higher A_gave value compared to the free ion value [Ru(III) = 54.3] suggest that the metal-ligands bonds are covalent.

The ESR spectrum of Cu(II) complexes, 16 and 17 are recorded both at room temperature and liquid nitrogen temperature. The LNT ESR spectrum of complex 14 shows nine distinct hyperfine lines indicating the presence of two non-equivalent nitrogen atoms bonded to Cu(II) ion. With the help of the spectra and using relevant equations, the parameters, like \( g_h, g_d, g_{ave}, A_g, A_{ave}, K_1, K_2, G, \alpha^2 \) and \( \beta^2 \) have been evaluated. The \( \alpha^2 \) and \( \beta^2 \) values are found to be 0.61, 0.63 and 0.68, 0.79 respectively for the two complexes. Since these values are less than 1.0 and close to 0.5, it may be concluded that the M-L bonds are covalent. Further, this is supported by the lower \( \lambda \)-values (346 and 418 cm\(^{-1}\)) compared to that of the free ion value (828 cm\(^{-1}\)) indicating the mixing of metal and ligand orbitals. The order \( K_1 > K_2 \), indicates that the preferred order of electronic energy levels in these complexes is \( 2B_{1g} < 2A_{1g} < 2B_{2g} < 2E_g \).

Based on the analytical data and spectral evidence, the following tentative structures (Structure I) have been proposed for the complexes.

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**References**
