Synthesis, characterization and ferromagnetic behavior of \([\text{Co}^{\text{III}}(\text{en})_2(\text{RC}_6\text{H}_4\text{NH}_2)]\text{I}_2\cdot\text{H}_2\text{O}\) complexes

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Mixed ligand cobalt(III) complexes containing aryl amine (RC6H4NH2) ligand have been synthesized using a modified route developed in this study. A wide range of complexes, \([\text{Co}^{\text{III}}(\text{en})_2(L)]\text{I}_2\cdot\text{H}_2\text{O}, (\text{where } L = \text{RC}_6\text{H}_4\text{NH}_2; R = m\text{-OMe, } p\text{-F, } \text{H, } m\text{-Me, } p\text{-Me, } p\text{-OEt and } p\text{-OMe})\) show promising reactivities and physical properties due to the presence of electron donating/acceptor groups in the aryl ligand. The complexes have been characterized by elemental analysis, FT-IR, UV-vis and powder X-ray diffraction patterns. FT-IR spectral data are compatible with trans-form of the complexes. Magnetic studies yield magnetic remanence \(M_r = 7.071 \times 10^{-3} – 3.069 \times 10^{-5}\) emu/g and intrinsic coercivity, \(-H_c = 141-1156\) Oe. Linear regression plot of \(M_r\) versus \(\sigma\) yields negative slope, implying that electron withdrawing group in \(\text{RC}_6\text{H}_4\text{NH}_2\) (\(\sigma > 0\)) enhances ferromagnetic character while the electron donating groups (\(\sigma < 0\)) reduce ferromagnetism. The study provides evidence that substitution at the aryl ligand, remote from the Co(III) center, effectively displays and imparts characteristic ferromagnetic properties. Cobalt(III) complexes containing \(\text{RC}_6\text{H}_4\text{NH}_2\) ligand illustrate a simple molecular fabrication technique, which can be suitably integrated into a system, to have some control on the behavior of metal complexes. A modified ferromagnetic character due to charge build up on the metal centre by ligating nitrogen atom, which in turn makes the molecule into a centre of systematic variation in magnetization, has been observed.

Keywords: Coordination chemistry, Ferromagnetism, Cobalt, Aryl amines

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Transition metal complexes with aromatic amines as ligands such as aniline, RC6H4NH2, and its derivatives have been known for many years. The physical properties of these compounds are often used as models in more complicated biological systems. Recently, aryl/alkyl amine-cobalt(III) complexes have been synthesized and structurally characterized by spectroscopic and X-ray crystallographic analysis; such complexes exhibit distortion in octahedral symmetry. In order to understand the substituent effects due to varying chemical structures of cobalt(III) complexes on the spectral, powder X-ray diffraction patterns and magnetic properties, a series of cobalt(III)-aryls containing electron-donating or withdrawing substituents attached in 3- and 4-positions in the aniline ring of the ligand have been synthesized.

Pazderski et al. reported\(^3\) the effect of auxiliary ligand in \(\text{trans-[Co(py)_3Cl_2]}\cdot 6\text{H}_2\text{O}\) and \(\text{mer-[Co(py)_3Cl_2]}\) complexes on the spectral properties including \(^{15}\text{N}\) NMR/\(^1\text{H}\) NMR. Synthesis of aryl amine cobalt(III) complexes is heavily dependent on appropriate conditions and has been unsuccessful due to the steric effect of both the existing chelate in the coordination sphere and incoming aryl ligand during substitution. Linear polyamines and aryl amines are of great interest\(^4\) from several perspectives due to systematic change in their substitution, redox reactions, and magnetic behavior, more interestingly, in biological systems. Similarly, metal complexes containing polyamine/N-alkyl ligands in Co(II)\(^5\) and Co(III)\(^6\) complexes illustrate the steric hindrance in original coordinating modes. Some of the modifications carried out in the ligated polyamine leading to N-benzylation\(^8\) of Co(III) complexes are scarce. However, they illustrate characteristic structural features in reactivities.

In this study, we have synthesized and characterized seven aryl amine-cobalt(III) complexes, \([\text{Co}^{\text{III}}(\text{en})_2(L)]\text{I}_2\) (where L = RC6H4NH2; R = m-OMe, p-F, H, m-Me, p-Me, p-OEt and p-OMe) to understand the geometrical distortion and the linear dependence of ferromagnetism due to the presence of aryl ligand in the coordination sphere of cobalt(III) complexes. The aniline ligand present in the coordination sphere imparts novel magnetic properties. Variations in the powder X-ray diffraction patterns have also been discussed.
Experimental

CoCl₂·6H₂O (99%), aryl amines (RC₆H₄NH₂) and KBr (spectral grade) were purchased from Sigma Aldrich. HI (AR), 1,2-diamino ethane (LR) and all other chemicals were purchased from SD. Fine Chemicals (India). All the solvents and 1,2-diamino ethane were distilled and purified before use. Water was triply distilled over an all-glass apparatus.

Elemental analyses were performed using an Elementar Vario EL III-Germany instrument. The FT-IR spectral investigations in the range 4000-400 cm⁻¹ were carried out on a Thermo Nicollet-6700 FT-IR instrument (KBr pellet method) and far-IR spectra were obtained using polyethylene pellet technique. The crystalline powders were mixed with polyethylene in a 1% (w/w) mixture and pressed into pellet at 10 ton pressure for 8 min. to obtain a transparent pellet, which was inserted in the apparatus to record vibrational spectrum in the range 400 to 50 cm⁻¹ with a resolution 1 cm⁻¹.

Electronic absorption spectral studies were carried out using Shimadzu (model 2450) double beam spectrophotometer with quartz cells with complex (2 × 10⁻³M) in neat water.

Magnetic measurements were carried out using vibrating sample magnetometer (VSM) in powder form on Lakeshore-7404 (sample vibration frequency 82.5 Hz, dynamic range (1 × 10⁻⁵) to 103 emu, max. field at 1” gap: 15 kOe). The VSM technique was used to observe the hysteresis curve for the compounds [CoIII(en)₂(RC₆H₄NH₂)₂]H₂O complexes were as follows: R = m-OCH₃; yield: 0.722 g, 72%. Anal.: Calc. (Found): C, 18.85 (19.10); H, 3.88 (3.20); N, 10.01 (9.82)% p-F; yield: 0.80 g, 80%. Calc. (Found): C, 17.43 (17.01); H, 3.51 (3.13); N, 10.19 (10.01)%. H; yield: 0.782 g, 78%. Calc. (Found): C, 17.91 (18.02); H, 3.76 (3.20); N, 10.46 (10.23)%. m-CH₃; yield: 0.764 g, 76%. Calc. (Found): C, 19.29 (19.03); H, 3.97 (3.58); N, 10.25 (10.02)%. p-CH₃; yield: 0.844 g, 84%. Calc. (Found): C, 19.29 (18.74); H, 3.97 (3.72); N, 10.25 (10.04)%. p-OCH₃; yield: 0.752 g, 75%. Calc. (Found): C, 20.16 (19.70); H, 4.09 (3.61); N, 9.82 (9.62). p-OCH₃; yield: 0.691 g, 69%. Calc. (Found): C, 18.85 (19.02); H, 3.88 (3.90); N, 10.01 (9.73)%.

Results and discussion

Micro elemental analysis data are in accordance with the formula, [CoIII(en)₂(RC₆H₄NH₂)₂]H₂O complex. The complexes were found to be trans-isomers by the synthetic method and spectral assignments. Trans-[Co(en)₂Cl₂]Cl + RC₆H₄NH₂ → trans-[CoIII(en)₂(RC₆H₄NH₂)₂]Cl₂ ligand replacement was followed using UV-vis repeated scan spectra which indicated a shift in λmax at 416.9 nm to a longer wavelength. A single low-energy absorption band at ca. 601 nm is characteristic of the trans-form.

IR spectra of [CoIII(en)₂(RC₆H₄NH₂)₂]H₂O complexes in the 3500-400 cm⁻¹ ranges closely resemble each other in absorption patterns. IR data of the complexes shows the peaks at 3500 to 3400 cm⁻¹, which may be attributed to the antisymmetric and symmetric ν(O-H) stretching modes of lattice-bound water. The stretching absorption bands at 1650-1620 cm⁻¹ confirm bending modes of ν(O-H) due to hydrogen bonding in the complexes, suggesting hydrated form of molecule. The considerable shift in the prominent antisymmetric ν(N-H) stretching modes at ~3318-3005 cm⁻¹ (metal-amine at ~3300 cm⁻¹) and deformation mode at ~1632-1497 cm⁻¹ (metal-amine ~1600 cm⁻¹) shows
bands represent metal charge transfer transitions, while lower energy bands can be assigned due to ligand-to-metal charge transfer at ~280 nm, ~344 nm, ~465 nm and 601 nm. The two intense bands in the UV region. These are interpreted on the basis of LCAO-MO theory to be charge transfer bands from p-orbitals of halide ion to mainly d^2 orbital of the cobalt(III) ion. The shorter wavelength transition \( p_\pi \rightarrow d^2 \) is centered at ~287 nm while the other \( p_\pi \rightarrow d^5 \) is centered at ~345 nm and the \( \pi \rightarrow \pi^* \) transition due to RC,HNNH ligand is at ~232 nm. High energy charge transfer band is obscured in some cases or such transition is not detected at this concentration\(^{17}\). Aniline systems show optical transition\(^{18}\) from HOMO to LUMO, \( \pi \rightarrow \pi^* \) at 250 nm. However, acceptor/donor groups attached to the ring alter the energies of LUMO/HOMO levels. Intensities of absorption due to d-d bands of \( \text{Co}^{3+}(en)_2(\text{RC}_6\text{H}_4\text{NH}_2)\text{I}^{2+} \) are parallel with that of magnitude\(^{19}\) of \( c \) for \( \text{Co}(en)(\text{NH}_3)_3\text{CN}^{2+} \) ion. It is reported that molar extinction coefficient of d-d band increases\(^{11}\) by a factor of about ten when \( X \) is substituted by Cl \( \rightarrow \) Br \( \rightarrow \) I. More importantly, a weak band at \( ca. \) 601 nm is characteristic of the trans structures. In addition, cobalt(III) complexes of lower symmetry containing aromatic amines exist preferably in trans-form and the cis-form is less probable\(^{11}\).

The complex ion, \( \text{Co}^{3+}(en)_2(\text{RC}_6\text{H}_4\text{NH}_2)\text{I}^{2+} \), shows two intense bands in the UV region. These are interpreted on the basis of LCAO-MO theory to be charge transfer bands from p-orbitals of halide ion to mainly d^2 orbital of the cobalt(III) ion. The shorter wavelength transition \( p_\pi \rightarrow d^2 \) is centered at ~287 nm while the other \( p_\pi \rightarrow d^5 \) is centered at ~345 nm and the \( \pi \rightarrow \pi^* \) transition due to RC,HNNH ligand is at ~232 nm. High energy charge transfer band is obscured in some cases or such transition is not detected at this concentration\(^{17}\). Aniline systems show optical transition\(^{18}\) from HOMO to LUMO, \( \pi \rightarrow \pi^* \) at 250 nm. However, acceptor/donor groups attached to the ring alter the energies of LUMO/HOMO levels. Intensities of absorption due to d-d bands of \( \text{Co}^{3+}(en)_2(\text{RC}_6\text{H}_4\text{NH}_2)\text{I}^{2+} \) are parallel with that of magnitude\(^{19}\) of \( c \) for \( \text{Co}(en)(\text{NH}_3)_3\text{CN}^{2+} \) ion. It is reported that molar extinction coefficient of d-d band increases\(^{11}\) by a factor of about ten when \( X \) is substituted by Cl \( \rightarrow \) Br \( \rightarrow \) I. More importantly, a weak band at \( ca. \) 601 nm is characteristic of the trans structures. In addition, cobalt(III) complexes of lower symmetry containing aromatic amines exist preferably in trans-form and the cis-form is less probable\(^{11}\).

Powder X-ray diffraction pattern of the trans-\( \text{Co}^{3+}(en)_2(\text{RC}_6\text{H}_4\text{NH}_2)\text{I}^{2+} \) complexes have not been reported previously. However, there are previous studies\(^{19,20}\) on cobalt-amine chloride and \( \text{Co}(\text{NH}_3)_3(\text{OH}_2)_3\text{I}_3 \). The unit cell parameters evaluated from powder X-ray diffraction patterns are given in Table 1. The \( d_{\text{sal}} \) and 20 values observed are found to be in good agreement with that of values indexed for monoclinic analogue of \( \text{Co}(en)_2\text{Cl}_2\text{ClO}_4 \) (JCPDS: 00-023-1605, 00-023-1606). The prominent peaks observed between 20 = 18.5 to 45º were matched with that of peaks of the reference\(^{21,22}\). Table 1 presents unit cell dimensions (\( a, b, c \) values), interfacial angles (\( \alpha, \beta, \gamma \)), cell volume and particle size \( <d> \) in nm. When iodide is replaced with RC,HNNH ligand in the coordination sphere of \( \text{Co}^{3+}(en)_2\text{I}_3 \), the particle size is expected to be enhanced, which is evident from the tabulated data. Thus, the X-ray diffraction pattern of cobalt(III) aryl amine complexes can be indexed with monoclinic system in comparison with analogous \( \text{[Co(en)Cl}_2]\text{ClO}_4 \).
Magnetic hysteresis loops are the experimental evidence, giving the most distinctive fingerprint of ferromagnetism. The VSM technique was used to observe the hysteresis curves of Co\textsuperscript{III}(en)\textsubscript{2}(RC\textsubscript{6}H\textsubscript{4}NH\textsubscript{2})\textsubscript{2}I\textsubscript{2}H\textsubscript{2}O complexes in dc magnetic field. The hysteresis loops of the cobalt(III) complexes were obtained by plotting moment/mass (emu/g) versus field (Oe). Hysteresis loops measured for the complexes imply the existence of ferromagnetic behavior. The intrinsic coercivity and remanent magnetization values calculated for the complexes from VSM analysis are listed in Table 2. The results indicate that all the trans-Co\textsuperscript{III}(en)\textsubscript{2}(RC\textsubscript{6}H\textsubscript{4}NH\textsubscript{2})\textsubscript{2}I\textsubscript{2}H\textsubscript{2}O complexes show ferromagnetic behavior with significant magnetization. A closer look at the magnetic data reveal very clearly that the remanent magnetization varies consistently, which is in tune with the nature of the complex ion, Co\textsuperscript{III}(en)\textsubscript{2}(RC\textsubscript{6}H\textsubscript{4}NH\textsubscript{2})\textsubscript{2}I\textsubscript{2}+. More precisely, it depends on the presence of the sixth ligand in the coordination environment, that is, R of RC\textsubscript{6}H\textsubscript{4}NH\textsubscript{2} ligand, which in turn depends on electron withdrawing/donating group attachment. Although, R is remotely placed with reference to the metal centre, the magnetic property depends shows the existence of some relationship with Hammet's substitution constant ($\sigma$).

The linear plot of remanent magnetization ($M_r$) versus Hammet's substitution constant $\sigma$ (Fig. 1) indicates that $M_r$ of trans-Co\textsuperscript{III}(en)\textsubscript{2}(RC\textsubscript{6}H\textsubscript{4}NH\textsubscript{2})\textsubscript{2}I\textsubscript{2}H\textsubscript{2}O complexes increases linearly with respect to an enhancement in Hammet constant as $M_r = 3.069 \times 10^3 - 7.071 \times 10^3$ emu/g when $\sigma = -0.268-0.115$ (Table 2). Further, intrinsic coercivity, $-H_c = 141-1156$ Oe indicates the existence of magnetic behavior in the complexes. The room temperature magnetic hysteresis loop measurements suggest that the cobalt(III) complexes are ferromagnetic and the magnetic character varies in tune with the basicity of the axial ligand as observed for some of the low spin iron(III) complexes\textsuperscript{22,23}. However, linear relationship between the magnetic properties of the complexes versus substituent in aryl ligand is more complicated than that anticipated earlier. Some investigations have proved correlation between demagnetization property

### Table 1 — Powder X-ray diffraction parameters for trans-Co\textsuperscript{III}(en)\textsubscript{2}(RC\textsubscript{6}H\textsubscript{4}NH\textsubscript{2})\textsubscript{2}I\textsubscript{2}H\textsubscript{2}O complexes\textsuperscript{a}

<table>
<thead>
<tr>
<th>R in aniline</th>
<th>Unit cell dimensions (Å)</th>
<th>Interfacial angle ($\beta$°)</th>
<th>Vol. (Å$^3$)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-OMe</td>
<td>a = 10.34, b = 7.98, c = 9.51</td>
<td>M = 99.12</td>
<td>V = 776.22</td>
<td>71</td>
</tr>
<tr>
<td>p-F</td>
<td>a = 10.94, b = 8.46, c = 8.12</td>
<td>M = 98.75</td>
<td>V = 742.58</td>
<td>89</td>
</tr>
<tr>
<td>H</td>
<td>a = 4.32, b = 8.20, c = 18.39</td>
<td>M = 99.86</td>
<td>V = 647.12</td>
<td>79</td>
</tr>
<tr>
<td>m-Me</td>
<td>a = 12.74, b = 8.20, c = 8.90</td>
<td>M = 98.94</td>
<td>V = 918.92</td>
<td>71</td>
</tr>
<tr>
<td>p-Me</td>
<td>a = 3.75, b = 28.47, c = 23.61</td>
<td>M = 98.92</td>
<td>V = 2487.02</td>
<td>89</td>
</tr>
<tr>
<td>p-OEt</td>
<td>a = 12.95, b = 7.65, c = 9.03</td>
<td>M = 98.86</td>
<td>V = 883.63</td>
<td>98</td>
</tr>
<tr>
<td>p-OMe</td>
<td>a = 13.68, b = 7.36, c = 9.83</td>
<td>M = 99.01</td>
<td>V = 976.81</td>
<td>87</td>
</tr>
</tbody>
</table>

\textsuperscript{a}$\alpha = 90°, \gamma = 90°; \theta = 10 - 70°; \text{ step scanning } 20 \text{ increments of } 0.02°; \text{ counting time } 5s/\text{step}; \text{ X-ray source } \lambda = 1.541 \text{ Å}; \text{ acceleration voltage } 50 \text{ kV with } 40 \text{ mA current.}$

### Table 2 — Magnetic characteristics obtained from vibrating sample magnetometer for trans-Co\textsuperscript{III}(en)\textsubscript{2}(RC\textsubscript{6}H\textsubscript{4}NH\textsubscript{2})\textsubscript{2}I\textsubscript{2}H\textsubscript{2}O complexes\textsuperscript{a}

<table>
<thead>
<tr>
<th>R in aniline</th>
<th>Hammett's substitution constant, $\sigma$</th>
<th>Intrinsic coercivity, $-H_c$ (Oe)</th>
<th>Remanent magnetization, $M_r \times 10^3$ (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-OC\textsubscript{H}\textsubscript{3}</td>
<td>+ 0.115</td>
<td>570</td>
<td>7.071</td>
</tr>
<tr>
<td>p-F</td>
<td>+ 0.062</td>
<td>708</td>
<td>4.530</td>
</tr>
<tr>
<td>H</td>
<td>0.000</td>
<td>415</td>
<td>6.040</td>
</tr>
<tr>
<td>m-CH\textsubscript{3}</td>
<td>- 0.069</td>
<td>248</td>
<td>3.167</td>
</tr>
<tr>
<td>p-CH\textsubscript{3}</td>
<td>- 0.170</td>
<td>1157</td>
<td>1.086</td>
</tr>
<tr>
<td>p-OC\textsubscript{H}\textsubscript{3}</td>
<td>- 0.250</td>
<td>141</td>
<td>0.861</td>
</tr>
<tr>
<td>p-OCH\textsubscript{3}</td>
<td>- 0.268</td>
<td>596</td>
<td>0.031</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Vibrating frequency 82.5 Hz; dynamic range (1x10\textsuperscript{-7}) to 103 emu; max. field at 1° gap: 15 kOe in dc magnetic field at 27°C.

Fig. 1 — Regression plot of remanent magnetization, $M_r$ (emu/g) versus Hammett’s substitution constant, $\sigma$, for trans-Co\textsuperscript{III}(en)\textsubscript{2}(RC\textsubscript{6}H\textsubscript{4}NH\textsubscript{2})\textsubscript{2}I\textsubscript{2}H\textsubscript{2}O complexes at 27°C, (slope = 61.11).
of the mixed ligand nicotinate N-oxide metal(II) complexes\textsuperscript{24}. Likewise there is a clear correlation between $d$-$d$ bond positions and electronic effects of the substituents. In addition, metal complexes with aryl amine have been reported to confirm the correlation of physicochemical properties of the complexes with the electronic nature of the substituents\textsuperscript{25-27}.

The above study shows that Co$^{III}$($en$)$n$(RC$_{6}$H$_{5}$NH$_{2}$)$^{2+}$ complexes are ferromagnetic and establish a linear dependence of remanent magnetization with respect to RC$_{6}$H$_{5}$NH$_{2}$ ligand in terms of Hammett's $\sigma$ constant. Linear regression analysis of $M_{r}$ versus $\sigma$ yields negative slope indicating that the electron withdrawing group in RC$_{6}$H$_{5}$NH$_{2}$ ($\sigma > 0$) enhances ferromagnetic character and that electron donating group in RC$_{6}$H$_{5}$NH$_{2}$ ($\sigma < 0$) reduces the ferromagnetism. Some of the Fe(III) and Cu(II) complexes are found to show the demagnetization\textsuperscript{28} effect whenever the ligand field strength is increased. Therefore, it can be concluded that coordination environment of the metal centre of a transition metal ion can greatly influence the ferromagnetic character of the complex.

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References