Regioselective fusion of aromatic di-amines to coordinated 2-(phenylazo)pyridine. An approach to the synthesis of new ligands with large denticity

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Metal mediated oxidative fusion reaction of aromatic di-amines to coordinated 2-(phenylazo)pyridine (pap) ligand in the cationic cobalt complex, [Co(pap)]^2+ affords green complexes of general formula [Co(L)_2][ClO_4] ([HL = 2-[(N-aryldiamino)phenylazo]pyridine). In this reaction one of the two amine functions of the di-amine reagent is fused regioselectively to ortho-carbon of the pendant phenyl ring of coordinated pap to yield a bischelating tridentate ligand while the second amine function remains a pendant and does not take part in the fusion reaction. The crystal structure of one of the representative cobalt complexes, [Co(L)_2][ClO_4] is reported. The structure analysis reveals the presence of two anionic ligands, each of which acts as an N,N,N-tridentate donor. Physicochemical properties of the cobalt complexes are reported. The ligands HL_2 - HL_5 are isolated from the corresponding cobalt complexes by their decomposition. These free ligands showed resolved ^1H NMR spectra. The resonance due to -NH and -NH_2 in these appeared near 10.5 δ and 4.5 δ, respectively. The ligand HL_3 was reacted with salicylaldehyde, which underwent Schiff-base condensation to result an extended ligand HL_2 in a high yield. The ^1H NMR spectrum of HL_2 showed the presence of a -CH resonance at 10.6 δ and the -OH resonance at 13.3 δ. FAB mass and ^1H NMR spectra of the newly synthesized organic ligands indeed confirm their formulations.

Introduction

Chemical transformations of organic substrates, coordinated to transition metal ions are important as these provide facile synthesis of many novel molecules that are otherwise difficult or even impossible to synthesize by conventional synthetic procedures. In these reactions the metal ions act as mediator, which in fact forms the basis of homogeneous catalysis. We have been interested in transition metal catalyzed organic transformations in the context of synthesis of new ligands, particularly those having large denticity so that these can bind several metal ions to form polymeric systems. Such polymeric systems are expected to produce electronically coupled materials. In the recent past we have reported the synthesis of a series of tridentate N-donors by regioselective amine fusion reaction to coordinated 2-(phenylazo)pyridine (Scheme 1).

The compound HL_3 readily loses a proton (pK_a = 8.5±0.1) and its conjugate base [L_3]^+ acts as an anionic tridentate donor whose coordination chemistry has been versatile with many novel features. In an attempt to synthesize multidentate

Scheme 1
polynucleating ligands, using this strategy, we now have started exploring the fusion of aromatic diamines to coordinated pap ligand. It is anticipated that the resultant compounds from such reactions would contain a free amine function, which might be useful for further expansion of denticity of the ligands. In this paper we report our results on the aforesaid amine fusion reactions using some chosen aromatic diamines as the reactants. The cobalt complexes as well as the organic ligands have been isolated and fully characterized. Single crystal X-ray structure of a representative cobalt complex is also reported.

Materials and Methods

The starting complex, [Co(pap)3](ClO4)2, was prepared17 by the reported procedure. Solvents and chemicals used for synthesis were of analytical grade. The supporting electrolyte tetraethyl ammonium perchlorate and solvents for electrochemical work were obtained as before. [CAUTION! Perchlorate salts of metal complexes are generally explosive]. Although no detonation tendencies have been observed, care is advised and handling of only a small quantity recommended.

Synthesis of [Co(L2)2](ClO4)

The compound [Co(pap)3](ClO4)2 (1 g, 1.24 mmol) was added to the melt of 1,2-diaminobenzene (5 g, 46.24 mmol) and heated on a steam bath for 1 h. The initial brown color changed to light green. The cooled mixture was thoroughly washed with diethyl ether and crystallization of the green product from dichloromethane-toluene mixture yielded [Co(L2)2](ClO4), 1 in 60% as green crystals. [Anal. Found: C, 55.15; H, 4.16; N, 18.92; Calcd. for C16H14N6: C, 55.55; H, 3.81; N, 19.06%. IR (KBr pellets): v (N=N) 1585, v (C=N) 1616, v (ClO4) 1116, 627 cm⁻¹].

Isolation of HL2

The compound [Co(L2)2](ClO4) (0.15 g, 0.20 mmol) was dissolved in ethanol (30 ml) and to it hydrazine hydrate (2 ml) was added. The green solution immediately became brown due to the reduction of Co(III) to Co(II). Yellow ammonium polysulphide (5 ml) solution was then added and the mixture was stirred for 30 min, at room temperature. The resulting orange-yellow solution was evaporated and then extracted with dichloromethane. It was finally purified on a silica gel preparative TLC using benzene-chloroform mixture (1:2) which on evaporation yielded orange crystals of HL2. [Yield, 50%; m.p. 156°C. FAB mass (M) 290. Anal. Found: C, 70.46; H, 5.22; N, 24.13; Calcd. for C17H13N6O: C, 70.58; H, 5.19; N, 24.22%. IR(KBr pellets): v (N=N) 1460, v (C=N) 1620 cm⁻¹].

Rest of the cobalt complexes and the corresponding ligands were synthesized similarly. Their yields and spectral characterization data are collected below:

[Co(L3)2](ClO4): Yield, 50%; Anal. Found: C, 49.46; H, 3.86; N, 21.92; Calcd. for C16H14N6O2ClCo: C, 49.71; H, 3.88; N, 21.75%. IR (KBr pellets): v (N=N) 1318, v (C=N) 1616, v (ClO4) 1116, 627 cm⁻¹.

HL4: Yield, 45%; m.p. 155°C. FAB mass (M) 291. Anal. Found: C, 65.86; H, 4.30; N, 28.80; Calcd. for C10H4N6Co: C, 66.21; H, 4.83; N, 28.97%. IR (KBr pellets): v (N=N) 1460, v (C=N) 1582 cm⁻¹.

Physical measurements

Elemental analysis was performed using a Perkin-Elmer 240C instrument. 1H NMR spectra were recorded in CDCl3 with a Bruker Avance DPX 300 spectrophotometer and SiMe4 as an internal standard. Melting points were determined with the help of capillary fitting Mel-Temp.II (Laboratory Devices Inc., USA) apparatus. A Shimadzu UV 2100 UV-vis spectrophotometer was used to record electronic spectra. Magnetic susceptibilities of samples were measured on a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. Electrical conductivity was...
measured by using a Systronics Direct reading Conductometer 304. Electrochemical measurements were performed at 298K under a dry nitrogen atmosphere on a PC controlled EG & G PAR model 273A electrochemistry system as described earlier. All potentials were referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contributions. The value of ferrocene-mercury couple under our conditions was 0.40V. FAB mass spectra were recorded at Mass Spectrometry Facility at the University of Bristol, UK.

Data collection for X-ray crystallography
X-ray quality crystals (0.37 X 0.28 X 0.12 mm³) of [Co(L̄)]ClO₄.CH₂Cl₂ were obtained by slow diffusion of a dichloromethane solution of the complex into toluene. The data were collected on a Bruker SMART CCD 1000 diffractometer, equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073Å). The crystal data are as follows:

Crystal structure formula C₃₅H₃₀N₁₀O₄CI₃CO, M = 819.97, triclinic space group, P-1 (no. 2), a = 10.957(3)Å, b = 12.696(3)Å, c = 14.479(3)Å, α = 82.709(5)°, β = 81.815(5)°, γ = 68.604(4)°, V = 1850.2(8)Å³, Z = 2, T = 293(2) K, μ = 0.734 mm⁻¹.

The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares techniques against F² using SHELXL-97. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed geometrically and positional parameters were refined using a riding model. Isotropic atomic displacement parameters for hydrogen atoms were constrained to be 1.2. A total of 8375 reflections were collected in the range 1.43 < θ < 23.29° of which 5264 were unique. Final R indices [I > 2σ(I)]: R1 (observed) = 0.0529, wR2 = 0.1308, R (all data): R1 = 0.1052, wR2 = 0.1564. The largest difference peak and hole are 0.601 eÅ⁻³ and -0.505 eÅ⁻³, respectively. The crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Centre (CCDC 200276).

Results and Discussion
The three di-amines, viz., 1,2-diaminobenzene, 2,6-diaminopyridine and benzidine were chosen as the reactants. It is now known that 1,2-diaminobenzene acts as a chelating ligand whereas benzidine behaves as a bridging ligand. However, the coordination of 2,6-diaminopyridine is virtually unknown and one might expect a trimetallc coordination as is observed in 2,2'-dipyridylamine.

![Image of molecular structures](image)

The above di-amines react with the brown cationic complex, [Co(pap)₃][ClO₄]₂ smoothly in air. The results are discussed below.

The amine fusion reaction
The brown complex [Co(pap)₃][ClO₄]₂ was reacted with the melt of 1,2-diaminobenzene at 160°C for an hour. The mixture became green within this period. Workup of the crude product and subsequent crystallization gave crystalline green cobalt(III) compound 1 as the major product (yield 60%). The cobalt compound, thus obtained, is diamagnetic and is a 1:1 electrolyte in acetonitrile. The ¹H NMR spectrum of this compound confirms fusion of an amine function at the ortho-carbon of cobalt-coordinated pap ligand. Characterization data of this cobalt complex are collected in Table 1. The ¹H NMR spectrum is in agreement with its X-ray structure (vide infra). Notably, each kind of proton of the coordinated anionic ligand [L̄]⁻ gave rise to one signal indicating that the two ligands in 1 are magnetically equivalent.

Figure 1 shows the ORTEP and atom numbering scheme for [1]⁺. The structure analysis of [Co(L̄)]ClO₄ reveals the presence of two anionic ligands, each of which acts as an N,N,N-tridentate donor with deprotonation of the secondary amine nitrogen, viz., N(14) and N(34). The ligand HL₂ is formed due to fusion of 1,2-diaminobenzene using one of its two amine functions to the pendant phenyl ring of coordinated pap ligand. The second amine function of 1,2-diaminobenzene remains uncoordinated. The geometry of the cobalt complex is meridional and the metal atom sits on an imposed C₂-axis bisecting the angles N(11)-Co(1)-N(14) and N(31)-Co(1)-N(34). The two azo nitrogen atoms of
Table I—Spectral and electrochemical data

<table>
<thead>
<tr>
<th>Comp.</th>
<th>( \delta \text{NH} )</th>
<th>( \delta \text{NH}_2 )</th>
<th>Aromatic Protons</th>
<th>Pyridyl Protons</th>
<th>( \lambda_{max} ), nm (^b) ((e/M^2\text{-cm}^{-1}))</th>
<th>( E_{1/2}) ((\text{V} vs \text{SCE}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>4.9</td>
<td>6.1–7.6</td>
<td>7.8–8.2</td>
<td>890(7961), 790(10435), 720(9390), 660(6450), 405(19065), 320(18710), 290(23580)</td>
<td>(1.19^a, 1.52^b, -0.45(0.12))</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>4.3</td>
<td>6.1–7.2</td>
<td>7.5–7.9</td>
<td>880(3920), 785(5270), 715(5032), 650(3985), 305(18620), 295(10050), 245(35685)</td>
<td>(0.50^a, 1.25^b, -0.50(0.11))</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>4.3</td>
<td>6.0–7.4</td>
<td>7.5–7.9</td>
<td>900(8750), 790(11825), 720(11375), 655(7500), 405(24600), 290(53550), 255(49200)</td>
<td>(0.88^a, 1.12^b, 1.25^b, 1.57)</td>
</tr>
<tr>
<td>H L(^2)</td>
<td>10.3</td>
<td>3.8</td>
<td>6.7–7.5</td>
<td>7.8–8.7</td>
<td>435(3835), 295(10190), 240(16755)</td>
<td>(0.53^a, 1.43^b, -1.14^b, -1.82^b)</td>
</tr>
<tr>
<td>H L(^3)</td>
<td>10.4</td>
<td>4.5</td>
<td>6.1–7.4</td>
<td>7.7–8.7</td>
<td>485(5355), 320(16615), 275(15015)</td>
<td>(0.82^a, 1.40^b, -1.17(0.09), -1.51^b)</td>
</tr>
<tr>
<td>H L(^4)</td>
<td>10.5</td>
<td>3.6</td>
<td>6.6–7.4</td>
<td>7.6–8.6</td>
<td>445(3635), 300(25735)</td>
<td>(0.57^a, 0.77^b, -1.24^b, -1.46^b)</td>
</tr>
<tr>
<td>H L(^5)</td>
<td>10.6</td>
<td>-</td>
<td>6.9–7.4</td>
<td>7.6–8.1</td>
<td>470(4410), 345(24860), 280(24920)</td>
<td>(1.04^a, -0.8^b, -1.17^b)</td>
</tr>
</tbody>
</table>

\(^a\)Solvent, CDCl\(_3\), SiMe\(_4\) as internal standard. \(^b\)Solvent CD\(_3\)CN. \(^c\)Broad, \(^d\)Shoulder. \(^e\)Conditions: solvent, acetoniitrile, supporting electrolyte, NEt\(_4\)ClO\(_4\) (0.1M); Working electrode, Platinum; reference electrode, SCE; solution concentration, \(10^{-3}\)M. \(^f\)Irreversible \(E_{1/2}\); \(^i\)Irreversible \(E_{pc}\).

Fig. 1—An ORTEP plot and atom numbering scheme for the cationic complex [Co(L\(^2\))\(_2\)].

the anionic tridentate ligands approach the metal center more closely (Table 2) than the other four bonds. For example, Co(1)-N(13) is 1.855(4) Å while Co-N(11) and Co-N(31) bonds are longer 1.935(4) Å and 1.940(4) Å respectively. This may happen either due to the geometric reason, i.e., for a bis chelating tridentate ligand forming two five member chelate rings or due to the extensive delocalization of charge along the ligand backbone of the anionic ligand [L\(^2\)].

We wish to note here that the M-N bond lengths in other metal complexes of N,N,N-donor systems are unequal and the M-N length for the middle nitrogen is usually the shortest. Delocalization of electronic charge in the present cobalt complex is evident from its bond distance data. Notably, the N=N azo distances in these complex are appreciably elongated. For example, the average of this bond length in 1 (1.295(5) Å) is longer than that in free [H\(_2\)pap][ClO\(_4\)] (1.258(5) Å). Moreover, the bond length N(azo)-C(phenyl) (av. 1.362(6) Å) is shorter than the value of 1.421(5) Å found for the corresponding distance in the salt [H\(_2\)pap][ClO\(_4\)]. Similarly, the amido nitrogen atoms of [L\(^2\)]\(^-\) bind to the phenyl group of pap at a shorter distance than is observed for a normal N-C(phenyl) single bond. These are all indicative of charge delocalization within the ligand framework. The shortening of M-N(azo) bonds in [I] results either through an increase in the electron density on N(azo) and concomitant increased basicity or through enhanced \(\pi\)-bonding capability of the more conjugated ligand.
Table 2—Selected bond length (Å) and angles (°) of [Co(L^2)_3](ClO_4)_2.

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>Co(1)-N(33)</th>
<th>N(11)-C(15)</th>
<th>N(14)-C(22)</th>
<th>Co(1)-N(33)</th>
<th>N(11)-C(15)</th>
<th>N(14)-C(22)</th>
<th>Co(1)-N(33)</th>
<th>N(11)-C(15)</th>
<th>N(14)-C(22)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(1)-N(13)</td>
<td>1.855(4)</td>
<td>1.394(7)</td>
<td>1.415(7)</td>
<td>Co(1)-N(13)</td>
<td>1.855(4)</td>
<td>1.394(7)</td>
<td>Co(1)-N(13)</td>
<td>1.855(4)</td>
<td>1.394(7)</td>
</tr>
<tr>
<td>Co(1)-N(11)</td>
<td>1.935(4)</td>
<td>1.297(5)</td>
<td>1.361(8)</td>
<td>Co(1)-N(11)</td>
<td>1.935(4)</td>
<td>1.297(5)</td>
<td>Co(1)-N(11)</td>
<td>1.935(4)</td>
<td>1.297(5)</td>
</tr>
<tr>
<td>Co(1)-N(31)</td>
<td>1.940(4)</td>
<td>1.356(6)</td>
<td>1.377(8)</td>
<td>Co(1)-N(31)</td>
<td>1.940(4)</td>
<td>1.356(6)</td>
<td>Co(1)-N(31)</td>
<td>1.940(4)</td>
<td>1.356(6)</td>
</tr>
<tr>
<td>Co(1)-N(34)</td>
<td>1.965(4)</td>
<td>1.415(7)</td>
<td>1.373(8)</td>
<td>Co(1)-N(34)</td>
<td>1.965(4)</td>
<td>1.415(7)</td>
<td>Co(1)-N(34)</td>
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<tr>
<td>C(18)-C(19)</td>
<td>1.375(10)</td>
<td>1.429(7)</td>
<td>1.397(7)</td>
<td>C(18)-C(19)</td>
<td>1.375(10)</td>
<td>1.429(7)</td>
<td>C(18)-C(19)</td>
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<td>1.429(7)</td>
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<td>C(19)-C(20)</td>
<td>1.373(9)</td>
<td>1.355(6)</td>
<td>1.378(7)</td>
<td>C(19)-C(20)</td>
<td>1.373(9)</td>
<td>1.355(6)</td>
<td>C(19)-C(20)</td>
<td>1.373(9)</td>
<td>1.355(6)</td>
</tr>
</tbody>
</table>

The other two diamines, viz., 2,6-diaminopyridine and benzidine also react similarly with the cobalt complex, [Co(pap)_3](ClO_4)_2. However the yields in these two cases are less than for 1,2-diaminobenzene. The reaction under consideration, releases protons. Addition of pyridine as a base thus facilitated the reaction. The cobalt complexes were purified using preparative TLC technique.

Spectral and redox properties of the cobalt complexes

All three cobalt complexes (1-3), obtained as above, are crystalline. The three ligands and their cobalt complexes are abbreviated as follows (Scheme 2).

The cobalt complexes are molecular, soluble in all common organic solvents and produce intense green solutions. The ¹H NMR spectra consisted of highly resolved resonance indicating the presence of a two-fold axis of symmetry in all the complexes. The free -NH₂ resonates between 4.3 and 4.9 δ. Rest of the aromatic proton signals appeared in the range 6.0 - 7.6 δ. Each of the cobalt complexes shows an envelope of four closely spaced transitions (Fig. 2) in their solution electronic spectra in the range 600-1000 nm. The intensities of these transitions are quite high. We assign these transitions as metal-to-ligand charge transfer (MLCT). The multiple nature of these transitions may originate from the lack of symmetry of the coordination environment as well as due to the presence of different acceptor levels in the extended azo-imine ligand. There are multiple high-energy transitions in the UV region, which are assigned to inter- or intra-ligand charge transfer.

The IR spectral data and the redox behavior of the cobalt complexes are similar to those observed earlier.

Fig. 2—Solution spectra of [Co(L²)₃](ClO₄)₂. I (—) (a) and HL² (—..) in acetonitrile (b).
The chemical reduction of the cationic cobalt complexes followed by precipitation of Co$^2+$ as CoS produced HL (HL$^2$-HL$^4$) in moderate yields. These were purified on preparative TLC plate and obtained as crystalline orange solids. These showed highly resolved $^1$H NMR in CDCl$_3$. The -NH resonance appears$^{27}$ as a broad signal near 10.5 $\delta$ and the -NH$_2$ protons resonate near 4.5 $\delta$. The $^1$H NMR spectrum of a representative, HL$^4$ is shown in Fig. 2. Of these three ligands, the ligand HL$^5$ reacts smoothly with salicylaldehyde to yield the corresponding Schiff base, (H$_2$L$^5$) in a moderate yield. The chemical reaction is shown in the following Scheme 3.

The $^1$H NMR spectrum of the schiff base, H$_2$L$^5$ is shown in Fig. 3. Interestingly the schiff-base, H$_2$L$^5$ shows$^{28}$ -CH and -OH resonance at 10.6 $\delta$ and 13.3 $\delta$ while the resonance due to -NH$_2$ protons is absent. All the ligands discussed above react instantaneously with transition metal ions. Indications are strong that these form polymetallic systems. Our work in this area is on and the results will be reported in due course.

Acknowledgement

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