Ferric-Chloride-Promoted Oxidation of *p*-Anisidine to an *N*-Substituted Phenazine Derivative − Structural Elucidation, Protic Equilibria and Coordination Chemistry of the Phenazine

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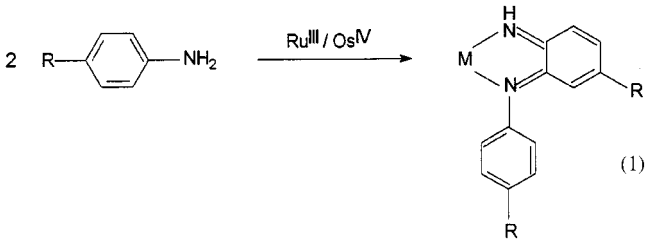
The reaction of hydrated ferric chloride and *p*-anisidine affords brown 6-*p*-anisyl-2-(*p*-anisylamino)-9-methoxy phenazine-3(4*H*)-*p*-anisylimine (LH) in moderate yield (35%). Plausible steps involved in this unusual fusion process are proposed. This phenazine spontaneously binds with H^+ to give a violet solution, p*K* for the reaction LH + $H^+ \rightleftarrows LH_2^+$ is 6.61 at 300 K. The protonated phenazine has been isolated as its chloride salt, $[LH_2Cl]$, the structure of which is described in authenticating the formation of LH directly from *p*-anisidine. The structural data reveal a planar dibenzo pyrazine moiety with an extensive delocalisation along the phenazine backbone. The protonation of LH occurs at the imine nitrogen. The spectral properties of both LH and $[LH_2]Cl$ are described. Both show well-resolved ^1H NMR spectra with four methyl resonances occurring in the range δ = 3.70 to 3.93. While $[LH_2]Cl$ shows two NH resonances at δ = 11.95 and 10.18, neutral LH displays only one such resonance at δ = 8.49. Aromatic proton resonances for these compounds appeared in the range δ = 5.79 to 8.04. The coordination abilities of the above phenazine were explored. It reacts spontaneously with $[M(aap)_2X_2]^{n+}$ (M = Ru^{II}, Os^{II}; aap = 2-(arylazo)pyridine; X = solvent, *n* = 2; X = Br^-, *n* = 0) to give cationic complexes of the general formula, $[M(aap)_2L]^+$ which were isolated as their perchlorate and bromide salts. These metal complexes were fully characterized. Their spectral properties indicate a bidentate anionic chelation of L^-, with deprotonation of the amine nitrogen. The complexes show multiple redox responses. The oxidised complexes are unstable and undergo chemical transformations. The reduction processes, on the other hand, are electrochemically reversible and presumably occur at the coordinated aap ligands.

Introduction

This work originated from our interest in metal-promoted oxidative dimerisation and polymerisation reactions of aromatic amines. In this respect, we have recently reported[1−3] the ruthenium(III)- and osmium(IV)-mediated *ortho* dimerisation of primary aromatic amines, $ArNH_2$, leading to *N*-aryl-1,2-diimino arenes [Equation (1)]. It may be relevant to add here that complexes of quinone-related 1,2-diimine ligands are of interest[4,5] in contemporary research and that *N*-substituted 1,2-diimino complexes of the above type were not possible to synthesise by conventional synthetic routes.

The above transformation is a combination of two major processes: oxidative *ortho* dimerisation of $ArNH_2$ and further oxidation of the resultant dimer would form the diimine ligand. Anodic oxidation of aromatic amines[6] associated with *para* coupling leading to *p*-benzidine or *p*-semidine are common. There are also examples of oxidation of



(1)

$ArNH_2$ to diazo compounds, Ar−N=N−Ar. Oxidative dimerisation with C−N bond formation, as described in Equation (1), however, was not known in the literature. This transformation occurs only in the presence of O_2, which acts as an oxidising agent. It is proposed that the metal mediates this transformation by holding the amine residues in a suitable juxtaposition and also by taking part in the redox processes. The unusual observations in the above cases of ruthenium and osmium prompted us to seek parallel developments using iron as the mediator. Interestingly, a completely different set of reactions occur with hydrated $FeCl_3$. In this report we disclose our results of the $FeCl_3$-mediated polymerisation reaction of *p*-anisidine to an *N*-substituted phenazine derivative. A literature survey revealed that the formation of an intense violet colour on addition of $FeCl_3$ to a solution containing *p*-anisidine was noticed[7] long ago, but the nature of product of the reaction was not determined.

Successful isolation and characterisation of the above phenazine together with its coordination chemistry invol-

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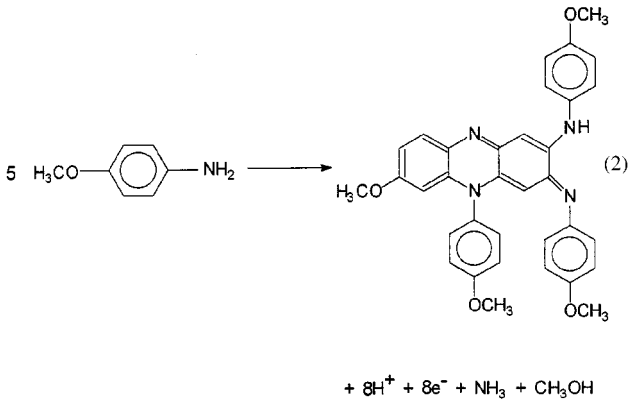
ving ruthenium and osmium constitute the major aspects of this report.

Results and Discussion

The Reaction

The reaction procedure consists of heating a mixture of hydrated $FeCl_3$ (100 mg) and a large excess of *p*-anisidine (2 g) at 120 °C in the air for one hour. The reaction occurs smoothly to produce an intense blue mixture. Usual work up (see Experimental Section) of the mixture followed by column chromatography (silica gel) afforded brown phenazine (LH) as the major product in 35% yield [(Equation (2)].



Beside the brown phenazine band, a mixture of blue and violet bands was also eluted with $CH_3CN/CHCl_3$ (1:4). We are as yet unable to obtain these in the pure state. This reaction only occurs neat and in the presence of O_2. It thus belongs to an example of the reaction class where catalytic activation[8] of dioxygen occurs by a transition metal ion.

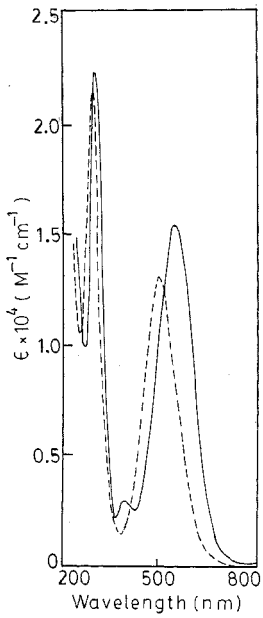


Figure 1. UV/Vis Spectra of LH (-------) and $[LH_2]Cl$ (− −) in acetonitrile

$$LH + H^+ \rightleftarrows LH_2^+ \cdots (3)$$

Characterisation of LH

The brown product isolated from the above reaction showed an intense FAB-MS peak at m/z = 558 confirming the formulation of the compound. The solution spectrum of LH in CH_3CN consists of a strong absorption at 505 nm

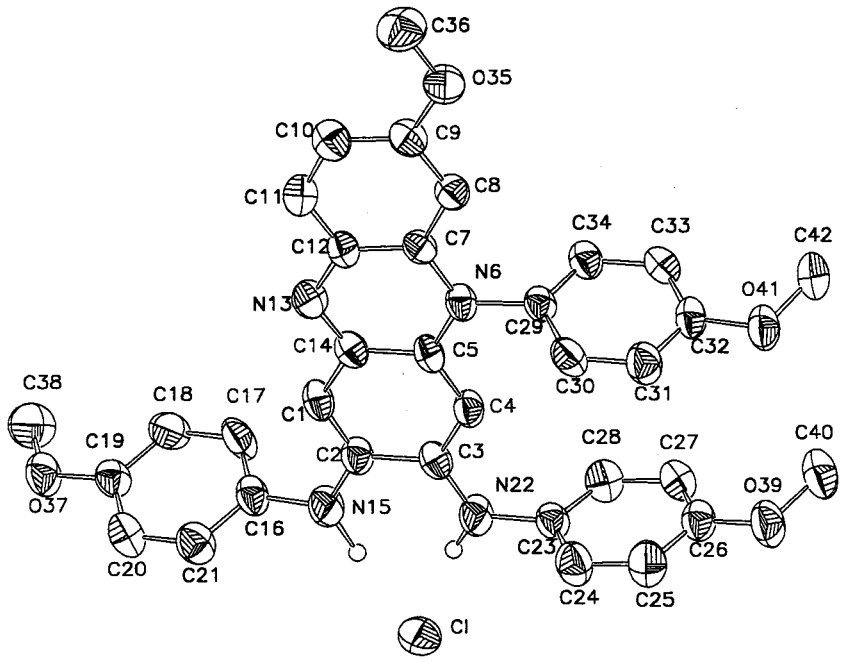
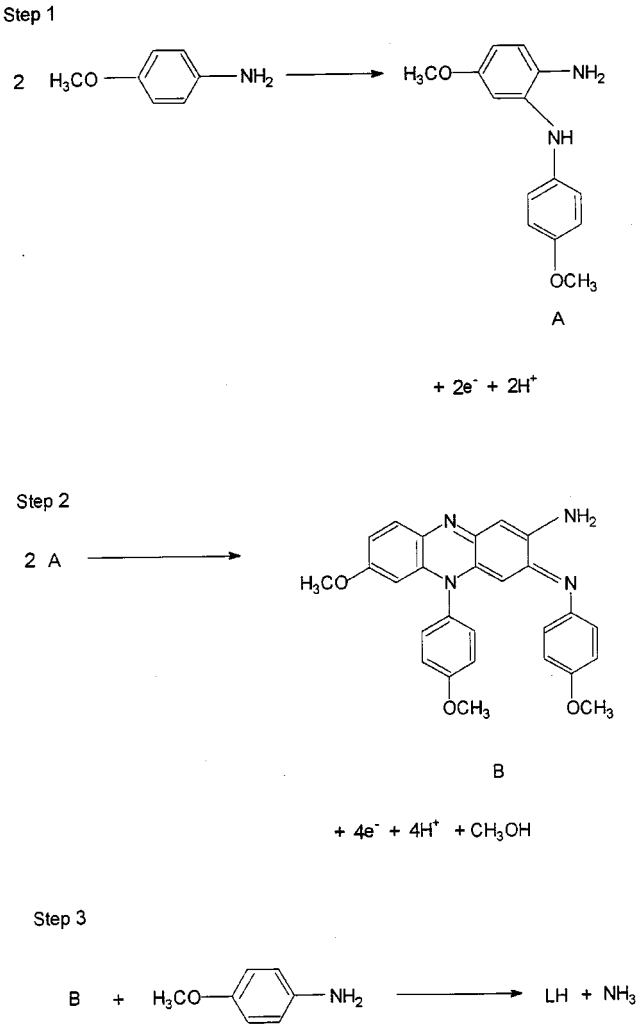


Figure 2. Molecular structure of $[LH_2]Cl$ showing the atom numbering scheme. Selected bond lengths [Å] : N(22)−C(3) 1.356(7), N(22)−C(23) 1.432(7), N(6)−C(5) 1.368(6), N(6)−C(7) 1.399(6), N(6)−C(29) 1.451(6), N(13)−C(14) 1.337(6), N(13)−C(12) 1.359(6), N(15)−C(2) 1.363(7), N(15)−C(16) 1.448(7), C(3)−C(4) 1.390(7), C(4)−C(5) 1.383(7), C(5)−C(14) 1.444(7), C(14)−C(1) 1.410(7), C(1)−C(2) 1.381(7), C(2)−C(3) 1.463(7)



Scheme 1. Plausible steps for the formation of phenazine

which may be attributed to extensive delocalisation (vide infra) along the phenazine backbone. Interestingly, the colour of the above solution became intense violet (λ_{max} 530 nm) on acidification. The spectra of these two are shown in Figure 1 and the spectral change as a function of $[H^+]$ is submitted as supplementary material (Figure S1). There is a sharp isosbestic point at 508 nm which indicates an acid-base equilibrium between LH and LH_2^+ [(Equation (3)]. The *pK* for this equilibrium reaction is 6.61±0.2 at 300 K. The chloride salt of the protonated phenazine, $[LH_2]Cl$ formed crystals suitable for X-ray structure determination. X-ray structure analysis[9] was used to authenticate the formation of $[LH_2]Cl$ and hence LH from a previously unknown reaction. A view of the molecule is shown in Figure 2, which indeed confirms the formation of a substituted phenazine with several C−N bond-formation processes.

The overall transformation is an 8 e^- + 8 H^+ transfer process and is accompanied by the elimination of one mol each of CH_3OH and NH_3. Oxidative dimerisation of *ortho* substituted aromatic amines, for example 1,2-diamino benzene or 2-amino phenol are documented in the literature.[8,10−11] These dehydrogenation processes proceed via radical intermediates[8,10b] which have been detected by EPR spectroscopy. It is proposed that the first and key step of *p*-anisidine → LH transformation is the dimerisation of the monoamine to produce *N*-aryl-1,2-diamino arene. This proposal is based on our results of the ruthenium- and osmium-promoted dimerisation reaction of *p*-anisidine. In those cases, however, the *N*-aryl diamine, once formed, undergoes dehydrogenation[2] to result in a coordinated 1,2-diimine [(Equation (1)]. In this case, once the *N*-aryl diamine is formed, it undergoes further dimerisation[11] and deamination processes to give LH. The plausible steps are shown in Scheme 1.

To the best of our knowledge, the formation of phenazine directly from a mono primary amine is not known. We wish to note here that identical reactions are also observed when neat *p*-anisidine is allowed to react with $CrCl_3$ or $RhCl_3$.

A close examination of the bond angles and distances of the salt $[LH_2]Cl$ reveals that the long chain, N15−C2−C1−C14−N13−C12−C11−C10−C9−C8−C7−N6−C5−C4−C3−N22 contains hybrid bonds. The ranges of bond lengths in this chain are C−C = 1.372 to 1.410Å and C−N = 1.337 to 1.399Å . Moreover, a least-square plane calculated through the 14 atoms of the dibenzo pyrazine fragment indicates that the skeleton is approximately planar; the largest deviation from the mean plane is 0.09Å. The planarity of the phenazine fragment, together with the bond length trends, indicates extensive delocalisation. This may be due to considerable contributions of the different resonance forms of the molecule. Furthermore, of the four substituents of the phenazine fragments, the two nitrogen atoms, *viz*. N15 and N22 deviate by 0.096 Å and 0.104 Å from the mean plane. The anisyl ring is almost perpendicular to the pyrazine ring. The torsion angle C5−N6−C29−C34 is 95.52°. This orientation minimises the steric interaction between *ortho* hydrogens *viz.* H30 and H34 and those on the phenazine, H4 and H8. Finally, it may be noted here that the crystal and molecular structure of $[LH_2]Cl$ is stabilised through[12] several hydrogen bonds.

Both LH and its conjugate acid $[LH_2]Cl$ show highly resolved ^1H NMR spectra (Figure 3). While there are two broad N−H resonances[13] at δ = 11.95 and 10.18 for $[LH_2]Cl$, the corresponding deprotonated compound LH showed only one broad resonance at δ = 8.49. The spectrum of the salt $[LH_2]Cl$ is better resolved and the resonances are shifted downfield from those for the corresponding neutral LH, as expected. The four methyl resonances appear in the range δ = 3.70 to 3.93, whereas the aromatic proton resonances are spread between δ = 5.79 and 8.04. Assignment of some of the resonances was not possible due to overlap of the resonances of unique protons. However, the H1 and H4 resonances in LH appear at δ = 6.18 and 5.79, respectively. The H1 signal appears as a doublet with *J* = 2.1 Hz. Irradiation of the signal at δ = 8.49 in LH results in the doublet at δ = 6.18 collapsing to a singlet, confirming that these two protons are magnetically coupled. These two resonances in the corresponding $[LH_2]Cl$ appear at δ = 6.38 and 6.24. Selected assignments

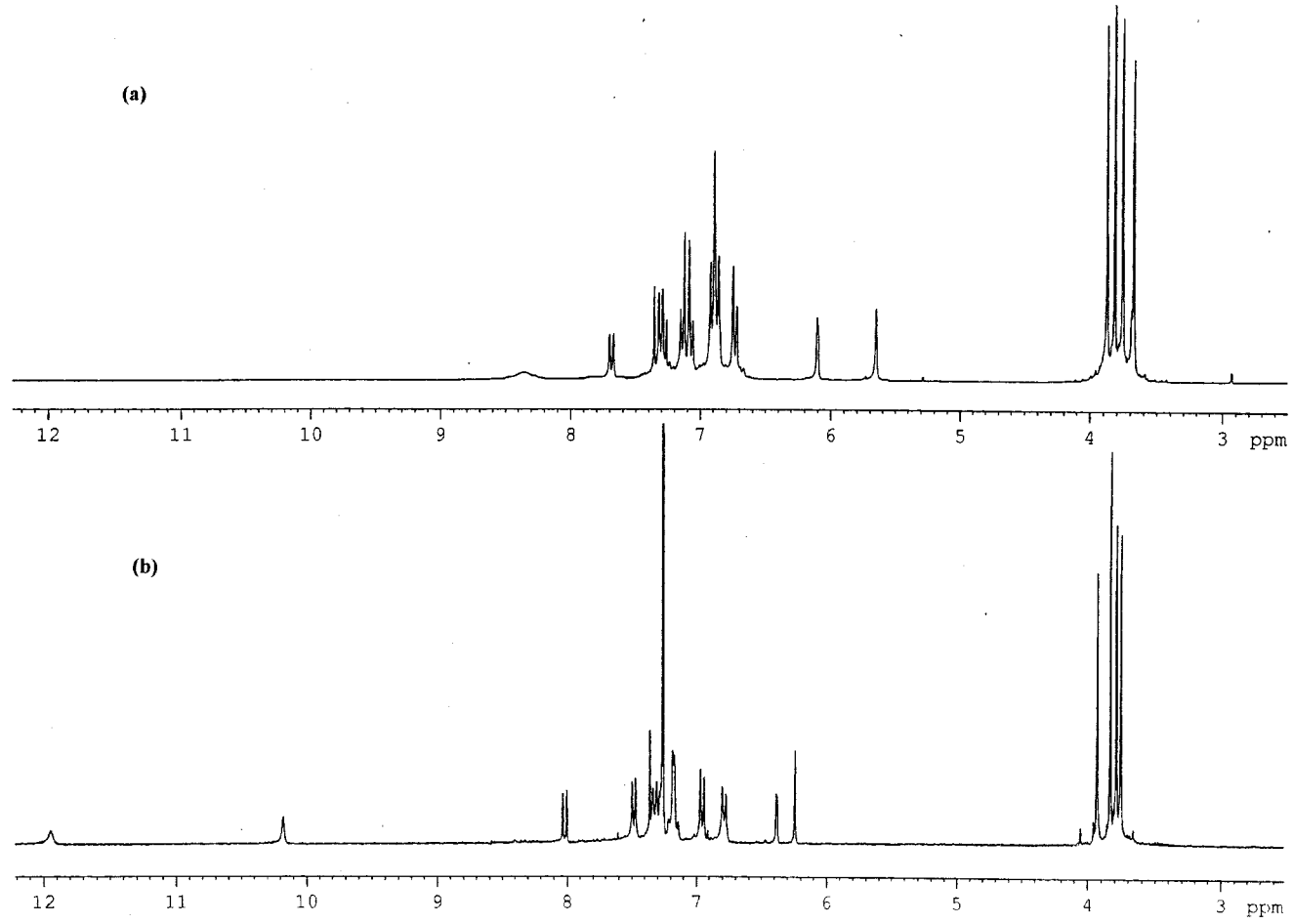


Figure 3. NMR spectra of (a) LH and (b) $[LH_2]Cl$ in $CDCl_3$

of the proton resonances are presented in the Experimental Section.

Binding of L to $M(aap)_2^{2+}$ moiety (M = Ru, Os)

The high affinity of the phenazine LH for H^+ led us to explore its coordination ability to transition metal ions. We chose $M(aap)_2^{2+}$ [M = Ru^{II} and Os^{II}, aap = 2-(arylazo)pyridine], as the possible binding sites. It may be relevant to note here that dipyrido phenazine complexes[14−16] of Ru^{II} and Os^{II} bind DNA and RNA by intercalation and represent an important class of molecular probes.

The compound LH reacts[17] smoothly with $[Ru(OH_2)_2(aap)_2]^{2+}$ in boiling methanol in the presence of a few drops of NEt_3 as base to yield a mixed *tris* chelate where L^- binds to Ru^{II} as a monoanionic bidentate ligand. Deprotonation of the amine nitrogen (N15), brought about by NEt_3, is essential for its chelation. The reaction of L^- with the dibromo analogue of osmium[18] under similar conditions proceeds at a much slower rate. The crude compounds were isolated as their perchlorate and bromide salts, respectively. Purification of the products was achieved by chromatography on silica gel column using different mixtures of $CHCl_3/CH_3CN$ as eluent. The mixed ligand complexes were obtained in high yields (75−80%). They are highly soluble in common organic solvents and their acetonitrile solutions behave as 1:1 electrolytes. The elemental analyses of these are consistent with the proposed composition $[M(aap)_2(L)]ClO_4$ (**1**).

Characterisation of $[M(aap)_2L]^+$

We employed several analytical methods to characterise the metal complexes, including ^1H NMR and UV/Vis spectroscopy, and cyclic voltammetry. The ^1H NMR spectrum of $[M(aap)_2(L)]^+$ contains several overlapping resonances in the aromatic region, owing to the presence of a large number of unique protons in these complexes. In this respect, the methyl resonances have been particularly useful for assessing the identity of the metal complexes. The $[M(pap)_2L]^+$ complexes display four −OMe signals in the range δ = 3.57−3.89 originating from the phenazine ligand; the corresponding *m*-tap complexes $[M(tap)_2L]^+$, on the other hand, display two extra methyl resonances at δ = 2.08 and 2.06, confirming the presence of two tap ligands in these compounds (Figure S2). Two methyl signals from the two tap ligands were expected due to the unsymmetric nature of the phenazine ligand. The disappearance of N−H

resonances in these complexes also indicates coordination of phenazine through N15 and N22. The number of ^1H NMR signals in these complexes is greater than those observed in LH and $[LH_2]^+$. The two pairs of doublets and one pair of triplets above $\delta = 7.5$ are assigned[19] to the pyridyl proton resonances, which further confirms the presence of two aap ligands in these compounds.

The phenazine ligand LH in the presence of 1 mM OH^- shows two intense transitions in the range 800−250 nm. One of these appears in the visible range at 490 nm while the other transition occurs at 280 nm. The solution colour of $[Ru(aap)_2L]^+$ is red-violet whereas that of the corresponding osmium analogue is blue-violet. The solution spectrum of the ruthenium complex consists of an intense transition at 545 nm. This transition is associated with at least two additional ill-defined shoulders occurring at longer wavelengths. The spectra of the corresponding osmium complexes showed multiple absorption peaks in the visible range. Each of them shows a transition at 790 nm and two more closely spaced transitions at 625 and 580 nm are also observed. The bivalent ruthenium and osmium complexes of aap, in general, display intense transitions in the visible range which are assigned to metal to ligand charge transfer (MLCT) transitions.[17−18] The number of absorption peaks in mixed ligand complexes varies depending on the presence of different acceptor orbitals. In the present complexes, the phenazine ligand itself has very intense visible range transition. Therefore, multiple transition possibilities,[20,21] originating from intra-ligand as well as MLCT transitions, exist in these complexes. The spectral data are collected in Table 1.

Table 1. Electronic spectral data

Compound	λ_{max}/nm(ε/M^{-1}cm^{-1})[a]			
LH	495(13110)	285(21230)		
LH_2Cl	540(15280)	390(2530)	290(22390)	
L^-[b]	575[c]	490	280	
$[Ru(pap)_2L]ClO_4$	555(18780)	340[c](21670)	295(28100)	
$[Ru(tap)_2L]ClO_4$	545(16900)	340[c](19400)	300(24520)	
$[Os(pap)_2L]Br$	790(5900)	625(12710)	580(12840)	310(21220)
$[Os(tap)_2L]Br$	785(5680)	620(12220)	570(11990)	315(22010)

[a] Solvent: acetonitrile. − [b] Qualitative spectrum generated by the addition of aqueous NaOH (in excess) to an acetonitrile solution of LH. − [c] Shoulder.

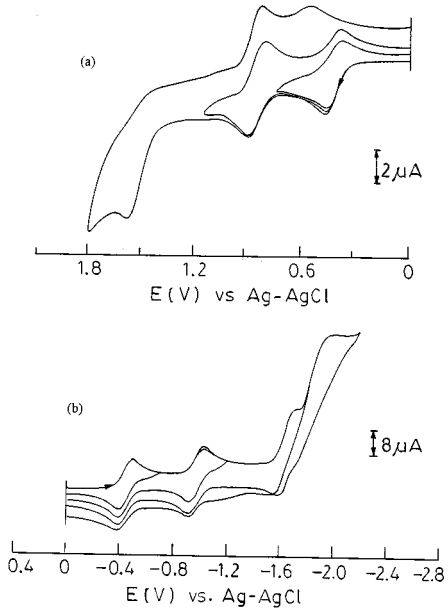


Figure 4. Cyclic voltammogram of $[Ru(m\text{-tap})_2L]ClO_4$; (a) anodic scan and (b) cathodic scan

Redox Properties

We employed cyclic voltammetry to determine the redox properties of the above ruthenium and osmium complexes. Figure 4 shows the multiple reduction waves of $[Ru(m\text{-tap})_2L]^+$ and the voltammetric data for all the complexes are collected in Table 2. The ruthenium complexes display three responses on the positive side of the Ag/AgCl reference. Of these, the couple with the lowest potential (0.45 *V*) is quasireversible with $i_{pa} > i_{pc}$, followed by a reversible couple at 0.97 *V*. Besides these, an irreversible anodic response of uncertain origin at 1.57 V was also observed. The first anodic response may be assigned to the oxidation of ruthenium(II) → ruthenium(III) in **1**. The next reversible response represents the ruthenium(II) → ruthenium(III) oxidation of a diimine analogue of **1** formed by the chemical transformation of electrogenerated $\mathbf{1}^+$. Ruthenium- and osmium-mediated electrochemical oxidation of the coordinated amine function are documented[17,22,23] in the literature. Keeping the above electrochemical transformations in mind, we examined whether the electrogenerated $\mathbf{1}^+$ would chemically be transformed to the diimine analogue of **1**. In practice, however, $\mathbf{1}^+$, produced by exhaustive electrolysis

Table 2. Electrochemical data[a]

	$E_{1/2}$/V(ΔE_p/mV)[b] Oxidation			Reduction			
$[Ru(pap)_2L]ClO_4$	0.47(70)	0.94(90)	1.56[c]	−0.38(90)	−0.89(100)	−1.63(150)	−2.07[d]
$[Ru(tap)_2L]ClO_4$	0.43(80)	0.85(90)	1.59[c]	−0.45(90)	−0.97(100)	−1.63(150)	−2.00[d]
$[Os(pap)_2L]Br$	0.68[e]			−0.39(80)	−0.88(60)	−1.57(60)	−2.27[d]
$[Os(tap)_2L]Br$	0.76[c]	0.91[c]	1.63[c]	−0.42(100)	−0.92(100)	−1.65(160)	−1.95[d]

[a] Conditions: solvent, acetonitrile; supporting electrolyte, NEt_4ClO_4 (0.1 M); working electrode, platinum for oxidation processes and glassy carbon for reduction processes; reference electrode, Ag/AgCl; solute concentration, 10^{-3} M. − [b] $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials; $\Delta E_p = E_{pa} - E_{pc}$. − [c] Irreversible E_{pa}. − [d] Irreversible E_{pc}. − [e] Irreversible E_{pa} with very large current.

of **1** at 0.70 V, yielded a mixture of compounds from which no pure product could be isolated. The responses in the case of osmium are more closely spaced and irreversible in nature.

The cathodic responses, on the other hand, are well defined. All the complexes showed three reversible couples along with a cathodic response of equal current (Figure 4) in the range −0.38 to −2.27 V. The coordinated ligand, pap, is known[17a] to undergo successive two-step one-electron transfer processes. Hence, these four responses may be attributed to the reductions of two aap ligands.

Conclusions

The direct formation of *N*-aryl phenazine (LH) from a mono aromatic primary amine, *viz*. *p*-anisidine, occurs through several oxidative carbon-nitrogen bond formation and cyclisation processes which otherwise do not occur with the free amine. This reaction is mediated by the ferric ion through the activation of O_2. This reaction is important in connection with the studies of chemical as well as electrochemical oxidations of primary aromatic amines. The coordination abilities of the anionic phenazine ligand $[L]^-$ have been explored. Our study of carbon-nitrogen bond formation processes using transition metal complexes as mediators is continuing.

Experimental Section

Materials: $RuCl_3 \cdot nH_2O$ was obtained from Arora Matthey and was digested three times with concentrated HCl before use. Solvents and chemicals used for syntheses were of analytical grade and used as received. The supporting electrolyte (TEAP) and solvents for electrochemical works were obtained as before.[17] $[Ru(aap)_2(OH_2)_2](ClO_4)_2 \cdot H_2O$ and $[Os(aap)_2Br_2]$ were prepared by literature methods.[17b,18b]

Physical Measurements: A Shimadzu UV 2100 UV/Vis spectrophotometer was used to record electronic spectra. The IR spectra were recorded with a Perkin−Elmer 783 spectrophotometer. ^1H NMR spectra in $CDCl_3$ were recorded on a Bruker Avance DPX 300 spectrophotometer, with $SiMe_4$ as internal standard. A Perkin−Elmer 240C elemental analyser was used to collect microanalytical data (C, H, N). Electrochemical measurements were performed under a dry nitrogen atmosphere on a PAR model 273-A electrochemistry system as described earlier.[20] All potentials reported in this work are referenced to Ag/AgCl and are uncorrected for junction contribution. The pH measurements were made with a μ-pH System 361 Systronics pH meter, standardised with buffers 7.0 and 9.2. A 70% CH_3CN/H_2O buffer mixture was employed. Electrical conductivities were measured by using a Systronics Direct Reading Conductivity meter 304. FAB-MS was obtained from JEOL AX 500/DA 5050 model mass spectrometer having a 70 eV ion source and direct inlet temperature of 180 °C.

Syntheses of Ligands

6-*p*-Anisyl-2-(*p*-anisylamino)-3(4*H*)-*p*-anisylimine-9-methoxyphenazine, (LH): A large excess of *p*-anisidine (2 g, 16.20 mmol) was added to hydrated $FeCl_3$ (100 mg, 0.60 mmol) and the mixture heated at 120 °C for 1 h. A violet melt resulted which was then extracted with dichloromethane, filtered and purified on a silica gel column (diameter:1 cm, height: 50 cm) After elution of the unchanged *p*-anisidine with pure chloroform, an intense red-violet band was eluted with chloroform/acetonitrile (19:1). On evaporation of the solvent and subsequent crystallisation from dichloromethane/hexane solutions dark red-brown crystals were obtained. Yield: 35%. − IR (KBr): $\tilde{\nu}$ = 1600 cm^{-1} (C=N), 3300 (N−H). − ^1H NMR ($CDCl_3$): δ = 8.50 (s, N−H, H_{15}), 7.77 (d, H_{10}, J = 9 Hz), 6.18 (d, H_1, J = 2.1 Hz), 5.79 (s, H_4), 3.89, 3.83, 3.77, 3.70 (s, 3 H, OCH_3). − $C_{34}H_{30}N_4O_4$ (558.6): calcd. C 73.11, H 5.37, N 10.03; found C 73.57, H 5.6, N 10.08.

Protonated Phenazine $[LH_2]^+$: A mixture of LH (56 mg, 0.10 mmol), dissolved in dichloromethane (20 mL) and very dilute aqueous HCl (10 mL, 1:20) was shaken vigorously in a separating funnel. The violet organic layer was then washed with water, collected and dried over anhydrous Na_2SO_4. Dark crystals of $[LH_2]Cl$ were obtained by slow diffusion of toluene into a dichloromethane solution of the compound. Yield: 98%. − IR (KBr): $\tilde{\nu}$ = 1615 cm^{-1} (C=N), 3300 (N−H). − ^1H NMR ($CDCl_3$): δ = 11.95 (s, N−H, H_{22}), 10.18 (s, N−H, H_{15}), 8.02 (d, H_{10}, J = 9.0 Hz), 7.36 (s, H_8), 6.95 and 6.79 (d, 2 H, *ortho* C−H of the anisyl rings, J = 8.4, 8.7 Hz, respectively), 6.38 (d, H_1, J = 2.4 Hz), 6.24 (s, H_4), 3.93, 3.83, 3.79, 3.76 (s, 3 H, OCH_3). $-C_{34}H_{31}ClN_4O_4$ (595.1): calcd. C 68.62, H 5.21, N 9.41; found C 68.70, H 5.18, N 9.40.

Syntheses of Complexes

6-*p*-Anisyl-2-(*p*-anisylamino)-3[(4*H*)-*p*-anisyliminobis(2-arylazo)-pyridine]-9-methoxyphenazineruthenium(II) Perchlorate, $[Ru(pap)_2L]ClO_4$: $[Ru(pap)_2(OH_2)_2](ClO_4)_2 \cdot H_2O$ (0.10 g, 0.13 mmol) and LH (0.08 g, 0.14 mmol) were dissolved in methanol (20 mL) and a few drops of NEt_3 added to the mixture. This reaction mixture was then heated at reflux for three hours. The colour of the solution became blue violet. The resulting solution was evaporated to dryness in a water bath and the crude product was purified on a silica gel column. Bands of different colours were first eluted with $CHCl_3$. Unreacted phenazine was then eluted with $CH_3CN/CHCl_3$ (1:12). Finally, an intense blue violet fraction was eluted with $CH_3CN/CHCl_3$ (1:6). After evaporation of solvent and subsequent recrystallisation from dichloromethane/hexane mixture, dark crystals of $[Ru(pap)_2L]ClO_4$ were obtained. Yield: 75%. − IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1}(C=N), 1290 (N=N), 1100, 630 (ClO_4). − ^1H NMR ($CDCl_3$): δ = 3.84, 3.76, 3.72, 3.57 (OCH_3). − $C_{56}H_{47}ClN_{10}O_8Ru$ (1124.6): calcd. C 59.81, H 4.18, N 12.46; found C 59.76, H 4.20, N 12.42.

The corresponding ruthenium compound of 2-(*m*-tolylazo)pyridine was prepared using the same procedure except that $[Ru(mtap)_2(OH_2)_2](ClO_4)_2 \cdot H_2O$ was used instead of $[Ru(pap)_2(OH_2)_2](ClO_4)_2 \cdot H_2O$. Yield: 75%. − IR (KBr): $\tilde{\nu}$ = 1600 cm^{-1}(C=N), 1290 (N=N), 1100, 630 (ClO_4). − ^1H NMR ($CDCl_3$): δ = 3.89, 3.84, 3.80, 3.64 (OCH_3), 2.08, 2.06 (CH_3). − $C_{58}H_{51}ClN_{10}O_8Ru$ (1152.6): calcd. C 60.44, H 4.43, N 12.16; found C 60.68, H 4.56, N 12.15

6-*p*-Anisyl-2-(*p*-anisylamino)-3[(4*H*)-*p*-anisyliminobis(2-phenylazo)-pyridine]-9-methoxyphenazineosmium(II) Bromide, $[Os(pap)_2L]Br$: This compound was synthesized by allowing $[Os(pap)_2Br_2]$ (0.10 g,0.14 mmol) to react with phenazine (0.08 g,0.14 mmol) in boiling 2-methoxyethanol under N_2 atmosphere for five hours, using Na_2CO_3 as base. The solution was then evaporated to dryness and the solid residue dissolved in chloroform and subjected to column chromatography on a silica gel bed. After elution of the unchanged phenazine with $CH_3CN/CHCl_3$ (1:12), an intense blue-

violet fraction was eluted with $CH_3CN/CHCl_3$ (1:6). Solvent evaporation followed by recrystallisation from dichloromethane/hexane mixture afforded dark crystalline $[Os(pap)_2L]ClO_4$. Yield: 75%. – IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1} (C=N), 1280 (N=N). – ^1H NMR ($CDCl_3$): δ = 3.86, 3.83, 3.81, 3.66 (OCH_3). – $C_{56}H_{47}BrN_{10}O_4Os$ (1194.2): calcd. C 56.32, H 3.93, N 11.73; found C 56.40, H 3.96, N 11.73.

The osmium compound of 2-(*m*-tolylazo)pyridine was prepared by the same procedure except that $[Os(m\text{-}tap)_2Br_2]$ was used instead of $[Os(pap)_2Br_2]$; yield 80% . – IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1} (C=N), 1285 (N=N). – ^1H NMR ($CDCl_3$): δ = 3.84, 3.82, 3.79, 3.63 (OCH_3), 2.03, 2.01 (CH_3). – $C_{58}H_{51}BrN_{10}O_4Os$ (1222.2): calcd. C 57.05, H 4.18, N 11.47; found C 57.50, H 4.16, N 11.94

Crystallographic Data: X-ray quality crystals (0.4 × 0.3 × 0.3 mm) of $[LH_2^+]Cl$ were obtained by slow diffusion of a dichloromethane solution of the compound into toluene. Cell parameters were obtained by least squares fits of 25 machine-centred reflections. Data were collected (1.67 ≤ 2θ ≤ 22.52°) on a Nicolet R3m/V diffractometer (295) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Two check-reflections measured after every 198 reflections showed no significant changes in intensity over 25 h. Data were corrected for Lorentz-polarisation effects. Of the 3948 reflections collected 3870 were unique (R_{int} = 0.0337) and 3867 reflections satisfying [$I > 2\sigma(I)$] were used for structure solution by direct methods and refined[9] by least-squares on F^2 using SHELXL93.The crystal data are collected in Table 3.

Table 3. Crystallographic data

Empirical formula	$C_{34}H_{31}ClN_4O_4$
M	595
Crystal system	Triclinic
Space group	*P*1(bar)
a/Å	8.651(6)
b/Å	12.768(6)
c/Å	14.106(7)
α/deg	80.71(4)
β/deg	83.96(5)
γ/deg	74.31(5)
U/$Å^{-3}$	1477.30(15)
Z	2
D_c/gm·cm^{-1}	1.338
R	0.0624
*wR*2	0.1406

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