

Synthesis, Characterisation and Electrochemistry of Some Stable Ruthenium(II) Complexes of the Bidentate NS Chelating Ligand 1-Amino-2-thiomethylbenzene

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Ruthenium(II) complexes of the bidentate aminothioether ligand, 1-amino-2-thiomethylbenzene (atb), have been synthesised by the direct reaction of atb with different ruthenium-containing starting materials. The complexes are of the type $\text{Ru}(\text{atb})_2\text{X}_2$ [$\text{X}=\text{Cl}$ (1), $\text{X}=\text{Br}$ (2)], $[\text{Ru}(\text{atb})_2(\text{PPh}_3)\text{Cl}]\text{Cl}$ (3) and $\text{Ru}(\text{atb})(\text{bpy})\text{Cl}_2$ (4), and have been characterised by elemental analysis, IR, UV–VIS and NMR spectroscopy. Contrary to the corresponding Ni^{II} , Pd^{II} , Pt^{II} and Cu^{II} complexes with the same ligand, these Ru^{II} complexes do not suffer demethylation on refluxing in DMF. Their electrochemical behaviour was examined by cyclic voltammetry using a glassy carbon working electrode and an Ag/AgCl electrode as reference.

The coordination chemistry of ruthenium ligated to mixed hard–soft nitrogen–sulfur chelating donors was a highly interesting but surprisingly ill explored area until the last decade or so.^{1,2} However, it is currently receiving the attention of coordination chemists, biochemists and even pharmacologists.^{3–9} Amino thioethers constitute a class of efficient N–S chelating ligands, but their ruthenium complexes are not well studied.^{10–13} The bidentate amino thioether, 1-amino-2-thiomethylbenzene (atb), has been reported to yield Ni^{II} , Pd^{II} and Pt^{II} complexes of the type $[\text{M}(\text{atb})_2\text{X}_2]$, $\text{X}=\text{Cl}$, Br or I , and $[\text{Pt}(\text{atb})_2][\text{PtCl}_4]$. These complexes underwent complete S-demethylation when refluxed in DMF.¹⁰ The copper(II) complexes $[\text{Cu}(\text{atb})_2\text{X}_2]$ ($\text{X}=\text{Cl}$ and Br) were found to be quite unstable.¹⁴ In some cases, as with copper(II)¹⁴ and gold(II),¹⁵ deprotonation of the coordinated amine also took place during complexation. The present work is a report on the preparation of some ruthenium(II) complexes of atb by direct reaction of the ligand with different ruthenium-containing starting materials (Fig. 1). The products were characterised by elemental analysis, by various spectroscopic and magnetic techniques and also by measurements of their conductance in solution. The electrochemical behaviour of these complexes has been explored by cyclic voltammetry. These complexes are

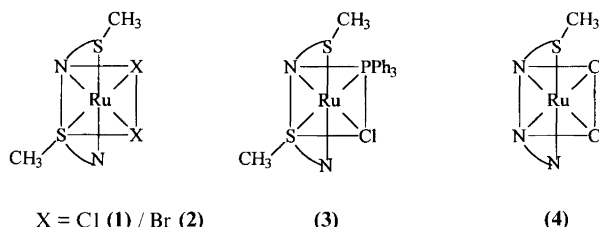


Fig. 1. Molecular structures of the complexes.

quite stable under laboratory conditions, and none of them suffers demethylation on refluxing in DMF.

Experimental

Materials. Commercial $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was received from Arora Matthey (India). $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ ¹⁶ and $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ ¹⁷ were prepared by published procedures. 2-Aminothiophenol was as received from Aldrich. Acetonitrile [E. Merck (India)] was freshly distilled over calcium hydride prior to the electrochemical experiments, the electronic spectral studies and the conductivity measurements. All other reagents were obtained from commercial sources and were used without further purification. Tetraethylammonium perchlorate was prepared by a published procedure.¹⁸

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Physical measurements. Elemental analyses were performed with a Perkin Elmer 240 CHNS/O analyser. Conductivity measurements of the complexes in acetonitrile were measured with a Systronics direct reading conductivity meter, model 304. Magnetic moments were measured at room temperature with a PAR vibrating sample magnetometer using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. IR and electronic spectra were recorded with a Perkin Elmer 783 spectrophotometer (as KBr pellets) and with a Shimadzu UV-VIS recording spectrophotometer. NMR spectra were recorded with a 300 MHz Bruker instrument using TMS as internal standard. The electrochemical data were obtained by cyclic voltammetry experiments with a Bio Analytical System (BAS) CV-27 electrochemical analyser and a BAS model X-Y recorder using a glassy carbon working electrode, a platinum auxiliary electrode and Ag/AgCl as reference electrode.

Preparation of the ligand (atb). 2-Aminothiophenol (10 g) was dissolved in dry EtOH (45 cm³) and small pieces of sodium (1.8 g) were slowly added during 1 h with constant stirring. Methyl iodide (11 g) was then slowly added with stirring, and the reaction mixture was finally poured into an equal volume of deoxygenated water, causing an oil to separate. The oil was extracted with diethylether, dried over fused CaCl₂ and distilled under reduced pressure. Yield: 65%, b.p. 114 °C/5 mm.

Preparation of the complexes.

[Ru(atb)₂Cl₂] (1). RuCl₃ · xH₂O, 0.261 g, 1 mmol, was dissolved in dry MeOH (40 cm³) in an N₂ atmosphere. The ligand, 0.417 g, 3 mmol, in dry MeOH (15 cm³) was added and the solution was stirred at room temperature for 8 h under an N₂ atmosphere. The solution was filtered, and the filtrate was concentrated to a small volume. The compound was then precipitated with diethyl ether. The product was filtered and washed with diethyl ether. The compound was twice dissolved in dry MeOH and precipitated with diethyl ether. The resultant solid was washed several times with diethyl ether and finally dried over fused CaCl₂. Yield: 40%.

[Ru(atb)₂Br₂] (2). To a solution of RuCl₃ · xH₂O, 0.261 g, 1 mmol, in dry MeOH (40 cm³) was added 1 g LiBr. The mixture was refluxed for 2 h and cooled to room temperature. The ligand, 0.417 g, 3 mmol, in dry MeOH (15 cm³) was added to the solution and the mixture was refluxed for 8 h under purified N₂ and then cooled to room temperature. The solution was concentrated to a small volume and the complex was precipitated with diethyl ether. The precipitate was washed with diethyl ether and purified as described for complex (1). Yield: 70%.

[Ru(atb)₂(PPh₃)Cl]Cl (3). [Ru(PPh₃)₃Cl₂], 0.192 g, 0.2 mmol, was dissolved in benzene (30 cm³), and the ligand (0.056 g, 0.4 mmol) was added. The mixture was refluxed under purified N₂ for 5 h. Some of the solvent was removed, and on treatment with diethyl ether, a gummy solid was obtained which was dried in vacuum.

The dry solid was dissolved in minimum volume of MeOH, and the compound was precipitated with diethyl ether and further purified like complexes (1) and (2). Yield: 60%.

[Ru(bpy)(atb)Cl₂] (4). [Ru(bpy)₂Cl₂], 0.152 g, 0.3 mmol, was dissolved in dry MeOH (40 cm³), and the ligand (0.125 g, 0.9 mmol) in dry MeOH (15 cm³) was added. The mixture was refluxed under purified N₂ for 8 h and cooled to room temperature. The solvent was removed in a vacuum, and a small amount of MeOH (2 cm³) and CH₂Cl₂ (10 cm³) was added to dissolve the solid residue. The compound was precipitated with petroleum ether (60–80 °C). The product was washed with petroleum ether (60–80 °C) and purified by redissolving the solid in a MeOH-CH₂Cl₂ mixture and precipitated with petroleum ether. The final product was washed with petroleum ether and dried in a desiccator over CaCl₂. Yield: 70%.

Results and discussion

Chemical formulae of the synthesised complexes have been suggested from elemental analysis and IR data and are supported by their conductance values.¹⁹ Irrespective of the metal:ligand (RuX₃:ligand) ratio used in the preparation, the composition of the isolated complexes was always Ru(atb)₂X₂. Similar 1:2 metal to abt ratios were also observed in complexes 3 and 4. Thus, compounds 1 and 2, having the general formula Ru(atb)₂X₂ [X = Cl (1), Br (2)], should act as non-electrolytes in acetonitrile (Table 1). The IR spectrum of compound 1 exhibits two ν(Ru-Cl) bands at 310 and 320 cm⁻¹ which are absent in the IR spectrum of compound 2, the ν(Ru-Br) mode in 2 was outside the detection limit of our IR instrument (Table 2). This observation indicates that the two chloro ligands in 1 are *cis* to each other.¹¹ Compound 3, having the chemical formula [Ru(atb)₂(PPh₃)Cl]Cl, exhibits only one ν(Ru-Cl) band,¹⁶ at 325 cm⁻¹, and behaves as a 1:1 electrolyte in acetonitrile. Two ν(Ru-Cl) bands¹² are located at 340 cm and 365 cm⁻¹ in the IR spectrum of Ru(atb)(bpy)Cl₂ 4, which is a non-electrolyte. The asymmetric and symmetric stretching frequencies of the NH₂ group of the free ligand are observed at 3450 and 3350 cm⁻¹, respectively.

Table 1. Analytical and physical data of the complexes.

Complex	Found (calcd.) (%)			Conductance ^a / Ω ⁻¹ cm ² mol ⁻¹
	C	H	N	
Ru(atb) ₂ Cl ₂ (1)	37.73 (37.33)	4.21 (4.0)	5.90 (6.22)	28
Ru(atb) ₂ Br ₂ (2)	31.05 (31.16)	3.87 (3.40)	5.13 (5.14)	26
[Ru(atb) ₂ (PPh ₃)Cl]Cl (3)	53.23 (53.91)	4.76 (4.63)	3.77 (3.93)	24
Ru(atb)(bpy)Cl ₂ (4)	43.70 (43.68)	4.17 (3.64)	8.87 (8.99)	30

^aConductances were determined immediately after dissolving the compounds in acetonitrile.

Table 2. Important IR bands (in cm^{-1}) of the complexes.

Complex	$\nu(\text{NH})$, $\nu(\text{CH})^a$	$\delta(\text{NH}_2)$	$\nu(\text{Ru}-\text{Cl})$	Other frequencies
$\text{Ru}(\text{atb})_2\text{Cl}_2$ (1)	3450(br), 3150, 3050, 2920	1590	310, 320	1565, 1470, 1145, 460
$\text{Ru}(\text{atb})_2\text{Br}_2$ (2)	3420(br), 3150, 3050, 2920	1600		1550, 1470, 1150, 450
$[\text{Ru}(\text{atb})_2(\text{PPh}_3)\text{Cl}]\text{Cl}$ (3)	3400(br), 3160, 3050, 3010	1600	325	1555, 1475, 1090, 450
$\text{Ru}(\text{atb})(\text{bpy})\text{Cl}_2$ (4)	3400(br), 3050, 3000	1600	365, 340	1550, 1460, 1160, 460

^abr, broad.

All complexes exhibit a broad band centered at 3430 cm^{-1} and a sharp band at 3150 cm^{-1} in their IR spectra which indicate that no deprotonation of the NH_2 group of the ligand has taken place during complexation.¹⁵ The lowering of the frequencies is due to coordination from the nitrogen atom of the $-\text{NH}_2$ group to Ru^{II} . The strong $\delta(\text{NH}_2)$ band of the free ligand at 1610 cm^{-1} is found to be shifted to a lower value in the complexes. All these results confirm the involvement of the NH_2 group of the ligand in coordination to the ruthenium centre. In contrast to the deprotonation of the coordinated NH_2 group observed in complexes of 2-aminothiophenol with various other transition metal ions, the present complexes do not undergo such deprotonation. The aromatic $\nu(\text{C}-\text{H})$ are observed in the $3050\text{--}3000\text{ cm}^{-1}$ region. One $\nu(\text{C}-\text{H})$ band of the CH_3 group, appearing at 2920 cm^{-1} , indicates that no demethylation occurs during complexation. A medium intensity band at 460 cm^{-1} in the IR spectra of the complexes, which is absent in the free ligand, may be assigned to the $\nu(\text{Ru}-\text{S})$ mode.^{13,20} All complexes are diamagnetic at room temperature.

Electrochemistry. The redox behaviour of the complexes was studied by cyclic voltammetry in acetonitrile. Results are given in Table 3. Cyclic voltammograms of compounds 1–3 exhibit a quasireversible to irreversible

Table 3. Cyclic voltammetric results^{a,b} of the complexes in CH_3CN .

Complex	$E_{1/2}/\text{V}$ ($\Delta E_p/\text{mV}$)	
	Oxidation	Reduction
$\text{Ru}(\text{atb})_2\text{Cl}_2$ (1)	0.96 (325)	−0.81 (125)
$\text{Ru}(\text{atb})_2\text{Br}_2$ (2)	0.72 (200)	−0.66 (150)
$[\text{Ru}(\text{atb})_2(\text{PPh}_3)\text{Cl}]\text{Cl}$ (3)	1.05 (250)	−0.76 (125)
$\text{Ru}(\text{atb})(\text{bpy})\text{Cl}_2$ (4)	0.80 (100)	−0.825 (100),
	1.21 (E_{pc})	−1.50 (75)
	1.51 (E_{pc})	

^aWorking electrode, glassy carbon; reference electrode, Ag/AgCl ; $E_{1/2} = 0.5(E_{pc} + E_{pa})$; where E_{pc} and E_{pa} are cathodic and anodic peak potentials, respectively. ^bSupporting electrolyte 0.1 M TEAP; solute concentration 10^{-3} M, scan rate 50 mV s^{-1} . ^cPeak height of the couple compared with one-electron oxidation of $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ of *cis*- $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ under identical molar concentration and experimental conditions.

$\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ oxidation. The separation between the cathodic and anodic peak values, ΔE_p , is greater than the ideal Nernstian value of 59 mV and $i_{pc}/i_{pa} > 1$ indicates departure from the reversible behaviour; such values of ΔE_p are commonly observed in related types of complexes.^{11,21} The $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ couple of compound 3 has a higher value owing to its higher formal charge.²² The larger electronegativity of the chloro ligands makes the chloro compound 1 more difficult to oxidise than the corresponding bromo compound 2.^{8,23} Compound 4, containing a bipyridine moiety, undergoes a series of oxidations at positive potentials. Such examples have been reported previously.^{11,22} The complexes exhibit a quasireversible reduction between -0.65 and -0.85 V which may be a ligand (atb)-centered reduction. This has been verified by the experimental data from CV studies on $\text{Zn}(\text{atb})_2$. Complex 4 shows another reduction at -1.51 V which is attributed to the reduction of coordinated bipyridine.¹¹ An irreversible anodic wave at -1.3 V for compound 4 during the second and subsequent scans is probably due to product(s) formed during the first scan.¹¹

Electronic spectroscopy. The electronic spectra of the compounds exhibit sharp intense peaks in the UV region and a broad band in the visible region (Table 4). The broad band in the visible region is metal-to-ligand charge-transfer transition. The shoulder around 375 nm is a second MLCT band,^{11,24} presumably due to splitting of the t_{2g} level in the low-symmetry ligand field condition. In order to check whether the species in solution were identical with those in the solid state, the spectra of 1

Table 4. Electronic spectral data of the complexes in CH_3CN .

Complex	$\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon/\text{M}^{-1}\text{ cm}^{-1}$) ^a
$\text{Ru}(\text{atb})_2\text{Cl}_2$ (1)	234(3.88), 295(3.59), 642(3.33)
$\text{Ru}(\text{atb})_2\text{Br}_2$ (2)	234(4.22), 298(3.52), 380(sh)(3.08), 705(2.84)
$[\text{Ru}(\text{atb})_2(\text{PPh}_3)\text{Cl}]\text{Cl}$ (3)	232(4.43), 309(3.52), 374(sh)(2.95), 552(2.91)
$\text{Ru}(\text{atb})(\text{bpy})\text{Cl}_2$ (4)	216(4.44), 275(4.19), 374(3.28), 542(3.21)

^ash, shoulder. Electronic spectra were recorded immediately after dissolution of the complexes.

and **2** were also recorded as KBr discs. The spectral patterns were found to be quite similar.

¹H NMR spectroscopy. The NMR spectra of the ligand atb exhibits one CH₃ proton signal at δ 2.3 ppm and a broad signal centered at 4.1 ppm for NH₂ (Fig. 2). The phenyl protons give signals between δ 6.4 and 7.5 ppm. The NMR spectrum of complex **1** exhibits two different methyl signals, at δ 2.58 and 2.42 ppm,²⁵ whereas the bromo compound **2** exhibits two methyl signals at δ 2.60 and 2.42 ppm. The two methyl signals in all the complexes reflect their chemical non-equivalence and support the *cis* structure proposed for all these complexes. Both compounds have aromatic proton signals in the aromatic region. Compound **3** exhibits two CH₃ proton signals at δ 2.86 and 2.0 ppm,²⁵ while the aromatic proton signals are observed between δ 6.7 and 7.8 ppm. The two methyl signals are due to different environments of the two CH₃ groups which is possible only when PPh₃ and Cl are *cis*. The broad peak centered at δ 6.76 is due to NH₂ protons.²⁶ Compound **4** exhibits one CH₃ proton signal at δ 2.36 ppm, one NH₂ proton signal at δ 4.27 ppm and aromatic proton signals between δ 6.7 and 7.4 ppm. The presence of one methyl group per ligand molecule confirms that demethylation and deprotonation do not occur during complexation.

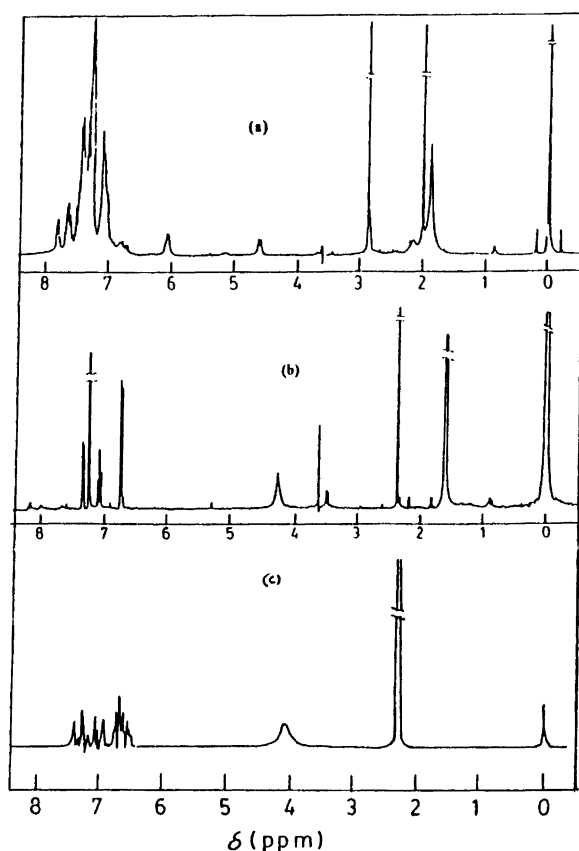


Fig. 2. ¹H NMR spectra of (a) [Ru(atb)₂(PPh₃)Cl]Cl, (b) Ru(atb)(bpy)Cl₂, and (c) the ligand (atb) in CDCl₃.

Conclusions

This work reports the synthesis of some ruthenium(II) complexes of an aminothioether which acts as a chelating bidentate ligand, and demonstrates (unlike most studies on transition metal complexes of thioether ligands) that no demethylation takes place. Binding sites of the ligand and their location inside the coordination zone of Ru^{II} have been substantiated from the analysis of IR and NMR data of the ligand and its complexes. Electrochemical reactivity in terms of oxidation and reduction was found to depend significantly on the nature of the co-ligands being present along with the NS (thioether) ligand.

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