

Sulphur-bridged ruthenium–molybdenum complexes: [(R-aapm)₂Ru(*m*-S)₂Mo(OH)₂]. Synthesis, spectroscopic and electro-chemical characterization. R-aapm = 2-(arylazo)pyrimidine

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Abstract. The reaction of *ctc*-[Ru(R-aapm)₂Cl₂] (**1**) with (NH₄)₂MoS₄ in aqueous MeOH afforded red-violet mixed ligand complexes of the type [(R-aapm)₂Ru(*m*-S)₂Mo(OH)₂] (**2a–2e**) [R-aapm = 2-(arylazo)pyrimidine, *p*-R-C₆H₄-N=N-C₄H₃NN, R = H (**2a**), Me (**2b**), Cl (**2c**), OMe (**2d**), NO₂ (**2e**)]. In complexes (**2a–2e**) the terminal Mo=S bonds of the MoS₄²⁻ unit get hydroxylated and the molybdenum ion is reduced from the starting Mo^{VI} in MoS₄²⁻ to Mo^{IV} in the final product. The solution electronic spectra exhibit a strong MLCT band at 550–570 nm in DCM. The ¹H NMR spectra confirms the geometry of the complexes as being that of *cis-trans-cis* isomers. Cyclic voltammograms show a Ru(III)/Ru(II) couple at 1.10–1.4 V, irreversible Mo(IV)/Mo(V) oxidations in the 1.66–1.72 V range, along with four successive reversible ligand reductions in the range –0.45–0.67 V (one electron), –0.82–1.12 V (one electron), –1.44–1.90 V (simultaneously two electrons).

Keywords. Ruthenium–molybdenum; 2-(arylazo)pyrimidine; sulphur bridged complexes; metal–ligand charge transfer.

1. Introduction

There has recently been significant research activity in the area of transition metal complexes of the tetrathiomolybdate anion. This attraction is due to its ability to form sulphur-bridged heteronuclear complexes of the type [(LL)₂M(*m*-S)₂MoS₂], [S₂Mo(*m*-S)₂M–MoS₂], [(LL)M(*m*-S)₂Mo(*m*-S)₂M(LL)] (M = Fe, Ru or Os),^{1–7,20,23} which are relevant for the functional and structural models of the active sites of the nitrogenase enzyme.^{4–6,22} The present work originates from my interest in studying the interaction of ruthenium arylazopyrimidine complexes *ctc*-[Ru(R-aapm)₂Cl₂]^{8–14} (**1**) [R-aapm = 2-(arylazo)pyrimidine, *p*-R-C₆H₄-N=N-C₄H₃NN] with (NH₄)₂MoS₄ in 1:1 aqueous MeOH, which has afforded red-violet mixed ligand complexes of the type [(R-aapm)₂Ru(*m*-S)₂Mo(OH)₂] (**2a–2e**), where the terminal Mo=S bonds become hydroxylated with the concomitant two-electron metal reduction,^{21,23,25,26} Mo^{VI}–Mo^{IV}. The MoS₄²⁻ unit is known to be sufficiently stable, individually as well as on coordination, and consequently the identity of the MoS₄²⁻ unit has been retained

in the earlier reported heteronuclear complexes.^{24,26} However, involvement of the ruthenium azoimidazole moiety facilitates (Mo(OH)₂) formation of the terminal Mo=S bonds in complexes. To the best of my knowledge this work demonstrates the first example of internal transformation of the MoS₄²⁻ unit on coordination.^{24–26} Owing to the biological involvement of pyrimidine, I was interested in synthesizing arylazopyrimidine.^{12–18} Ruthenium chemistry of (arylazo)pyrimidine (R-aapm, scheme 1, see §3 below) is known in some detail.^{9–15} Herein a detailed synthetic account of the formation of (**2a–2e**) complexes is reported and the spectroscopic and electrochemical properties of these complexes are investigated. Attempts to obtain a crystal of any of these complexes (**2a–2e**) have not been successful even after trying different methods of crystallisation.

2. Experimental

2.1 Materials

(NH₄)₂MoS₄ was purchased from Aldrich. RuCl₃·nH₂O was obtained from Arrora Matthey, Kolkata

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and was digested three times with concentrated HCl before use.^{8–12} 2-(Arylazo)pyrimidine was synthesized by the reported procedure.^{9,12,14} Commercially available silica gel (60–120 mesh) (Sisco Research Lab, India) was used for chromatographic separation. The purification of solvents for electrochemical and spectral work and of [*n*-Bu₄N][ClO₄] (TBAP) was done as described earlier.^{16–20} All other solvents and chemicals were reagent grade and were used without further purification.

2.2 Analytical measurements

Solution electronic spectra were recorded on a Jasco UV-VIS-NIR V-570 spectrophotometer. Microanalytical data (C, H, N) were collected using a Perkin-Elmer 2400 CHN elemental analyser. IR spectra were obtained using a Jasco 420 spectrophotometer (using KBr disks, 4000–200 cm⁻¹). The ¹H NMR spectra were obtained on a Bruker 300 MHz FT NMR spectrometer using SiMe₄ as internal reference. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10⁻³ M in MeOH. Electrochemical work was carried out using a PAR model 250 Versastat potentiostat/galvanostat with EG and G 270 software electrochemistry. All experiments were performed under an N₂ atmosphere at 298 K using a Pt-disk milli-working electrode and Pt-wire auxiliary electrode. All results were referenced to a saturated calomel electrode (SCE). Reported potentials are uncorrected for junction potential. K₄[Fe(CN)₆] was used as the standard showing the Fe(III)/Fe(II) couple at 0.17 V vs. SCE MeCN-0.1 (M) TBAP and 50 mV/s scan rate.

2.3 Synthesis of complexes

Synthesis of a representative complex is detailed below.

2.3a Preparation of di-*m*-sulpho[-bis-{2-(phenylazo)pyrimidine}ruthenium(II)-bis-(hydroxo)molybdenum(IV)], [(Haapm)₂Ru(*m*-S)₂Mo(HO)₂]. (2a): Aqueous AgNO₃ (0.06 g, 0.36 mmol) was added to a suspension of *ctc*-RuCl₂ (Haapm)₂ (0.1 g, 0.18 mmol) in MeOH (25 cm³) and the mixture was boiled under reflux for 30 min. After cooling, precipitated AgCl was filtered off using a G4 crucible. The volume of the solution was reduced to half of its original. Aqueous NaClO₄ (≈0.5 g in 2 cm³ H₂O) was added and kept at low temperature (0–5°C) overnight. The

compound thus precipitated was washed with cold H₂O and dissolved in MeOH. An aqueous solution of (NH₄)₂MoS₄ (0.05 g, 0.18 mmol) was mixed with the above MeOH solution and stirred at 60°C for 24 h. The dark solid was washed with cold H₂O and MeOH and dried in a vacuum desiccators over P₄O₁₀. The dry mass was then dissolved in a minimum volume of CH₂Cl₂ and chromatographed on a silica gel column (60–120 mesh). A red-violet band was eluted with toluene–acetonitrile (1 : 1, v/v), collected and slowly evaporated. The crystalline compound was collected in 45% yield (0.06 g).

All other complexes (**2b–2e**) were also prepared by following the above procedure and yields varied from 40–60%.

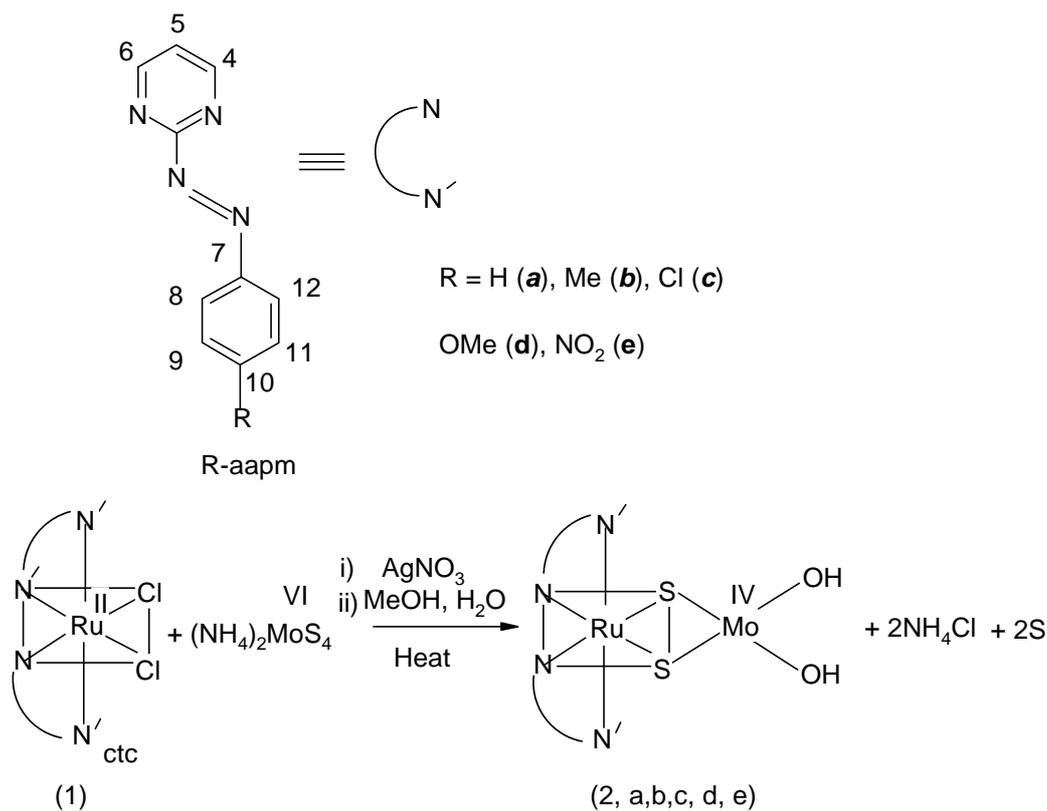
3. Results and discussion

3.1 Synthesis and formulation

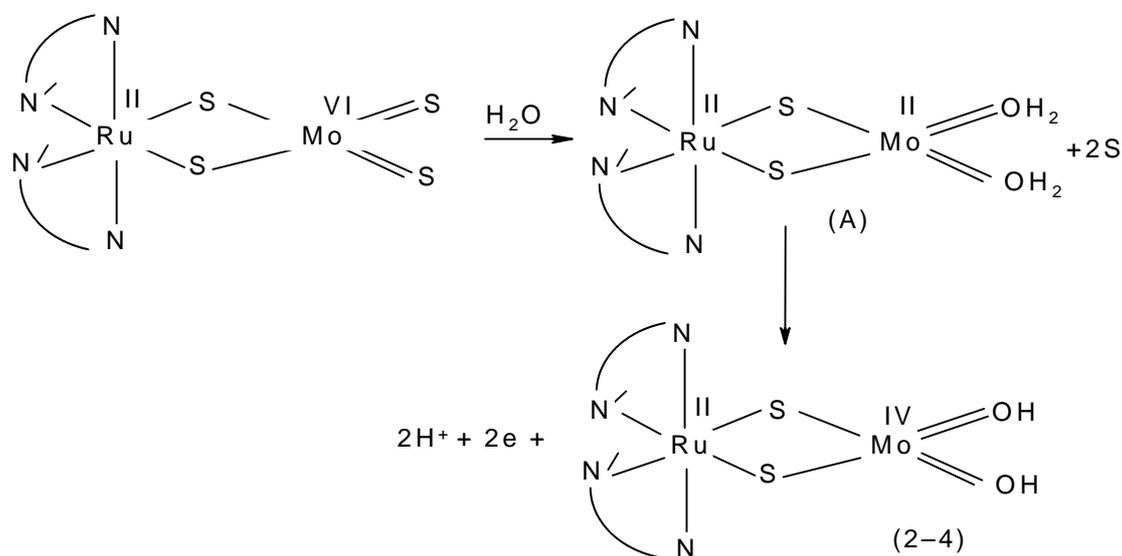
Ag⁺-assisted chloride substitution in *ctc*-Ru(R-aapm)₂Cl₂ (R-aapm = 2-(arylazo) pyrimidine) has been carried out in MeOH solution and the products have been isolated as their perchlorate salts [Ru(R-aapm)₂(EtOH)₂](ClO₄)₂. (NH₄)₂MoS₄ has been reacted with [Ru(R-aapm)₂(EtOH)₂](ClO₄)₂ in 1 : 1 methanol–water solution under refluxing conditions (scheme 1). The reaction mixture was kept at low temperature (0–5°C) overnight. The crystalline product was filtered and purified by chromatography.

The *ctc* isomer of the starting complexes, (**1**), is found to be the thermodynamically most stable product and the other two isolated isomers of (**1**), *ttt* (*trans-trans-trans*) and *ccc* (*cis-cis-cis*), are transformed into the most stable *ctc* isomer in high boiling xylene and DMF solvents.^{4–6} The complexes are sufficiently soluble in DMSO, chloroform and dichloromethane, but insoluble in benzene, toluene and hexane.

The formation of complexes (**2a–2e**) starting from (**1**) and MoS₄²⁻ is quite involved, as the reaction is associated with substitution, elimination and electron-transfer processes at the molybdenum centre. Since the formation of elemental sulphur from each Mo=S bond involves a 2-electron oxidation, the generation of totally four electrons possibly reduces molybdenum from the +6 oxidation state to the +2 oxidation state, followed by aquation in the presence of water as the first step of reaction.^{10–19} This is why water is needed in the reaction medium. As the +2 oxidation state of molybdenum is known to be



Scheme 1.



Scheme 2.

highly reducing in character, it is oxidized to Mo^{IV} via the reduction of H⁺ ions of the coordinated water molecules to hydrogen²⁴⁻²⁶ (product A, as intermediate, scheme 2).

The complexes show conductivity MeCN corresponds to a non-electrolyte. Solid state magnetic moment measurements at 298 K indicate that the complexes are uniformly diamagnetic and suggest

Table 1. Elemental analysis^a and IR spectroscopic^b data.

Comp.	Found (calc.)							IR ^b	
	C	H	N	S	Ru	Mo	O	-N=N-	-C=N-
[(Haapm) ₂ Ru(<i>m</i> -S) ₂ Mo(OH) ₂] (2a)	38.03 (38.23)	2.85 (2.98)	17.75 (17.86)	5.07 (5.10)	16.01 (15.58)	15.21 (15.34)	5.08 (5.10)	1350	1600
[(Meapm) ₂ Ru(<i>m</i> -S) ₂ Mo(OH) ₂] (2b)	40.06 (39.98)	3.34 (3.42)	16.99 (16.91)	4.86 (4.89)	15.33 (15.23)	14.57 (14.53)	4.88 (4.90)	1355	1606
[(Claapm) ₂ Ru(<i>m</i> -S) ₂ Mo(OH) ₂] (2c)	34.29 (34.22)	2.29 (2.23)	16.0 (15.89)	4.57 (4.52)	14.43 (14.33)	13.71 (13.66)	4.56 (4.55)	1353	1620
[(OMeR-aapm) ₂ Ru(<i>m</i> -S) ₂ Mo(OH) ₂] (2d)	38.21 (38.33)	3.18 (3.22)	16.21 (16.12)	4.63 (4.56)	14.62 (14.49)	13.89 (13.97)	9.26 (9.34)	1352	1630
[(NO ₂ aapm) ₂ Ru(<i>m</i> -S) ₂ Mo(OH) ₂] (2e)	33.29 (33.18)	2.22 (2.31)	19.42 (19.34)	4.44 (4.50)	14.01 (13.98)	13.31 (13.21)	13.32 (13.36)	1351	1624

^aCalculated values are in parentheses; ^bOn KBr plates

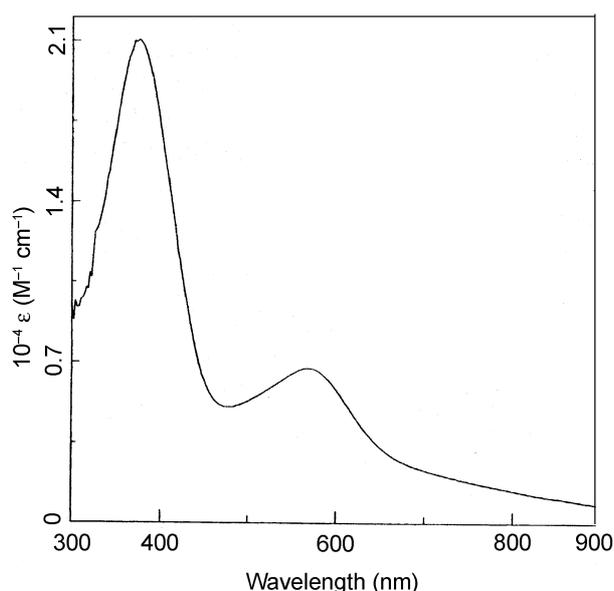


Figure 1. UV-Vis spectra of [(Haapm)₂Ru(*m*-S)₂Mo(OH)₂] (**2a**) in CH₂Cl₂ at 298 K.

low-spin-Ru^{II}, t_{2g}^6 , S=0, Mo^{IV} in a distorted tetrahedral arrangement setting the two metal electrons in the low-lying d_{z^2} orbital in a paired configuration. The composition of the complexes [(R-aapm)₂Ru(*m*-S)₂Mo(OH)₂] have been established by elemental analysis (table 1) and spectral studies.

3.2 Spectral studies

IR spectra (table 1) of the present series of compounds [(R-aapm)₂Ru(*m*-S)₂Mo(OH)₂] have been as-

signed comparing the spectra of the solvent complex [Ru(R-aapm)₂(EtOH)₂](ClO₄)₂.¹²⁻¹⁵ and free (NH₄)₂MoS₄. A moderately strong and broad band at ca ~3400 cm⁻¹ is assigned to the OH stretching frequency. However, the strong bands at 1600–1635 may be assigned to $\nu(C=N)$ and $\nu(N=N)$ appears at 1350–1360 cm⁻¹. The $\nu(N=N)$ of the free ligand appears at 1450–1420 cm⁻¹, which shifts to 1350–1360 cm⁻¹ on coordination in the complexes (**2a–2e**) due to strong $dp(Ru) \rightarrow p^*(L)$ back-bonding in the ground state of ruthenium(II), where $-p^*(L)$ is primarily dominated by the $-N=N-$ function.¹⁰⁻¹⁹

UV-Vis spectra of the complexes (in CH₂Cl₂) are dominant at 550–570 ($\epsilon \sim 10^4$), 500–520 ($\epsilon \sim 10^4$) and 350–390 ($\epsilon \sim 10^4$) nm (figure 1, table 2). On comparing with our previous results of ruthenium(II)-R-aapm we may conclude that the intense band in the visible region (550–570 nm) may be due to MLCT [$dp(Ru)-p^*(L)$] transitions where $-p^*(L)$ is believed to be primarily dominated by the LUMO of the azoimine chromophore.¹²⁻¹⁸ On the basis of their high intensities these first two bands are assigned as charge transfer in nature. In the complexes (**2a–2e**), the difference in potential between the first reduction couple and the reversible oxidation couple is 1.8 V, higher than that of the starting complexes (**1**), (~1.55 V). In view of the above observation it may be considered that the MLCT transition which occurs at 580 nm for the starting complex has been shifted to 560 nm in the complexes (**2a–2e**). The higher energy shoulder near 500 nm may be assigned¹³⁻¹⁷ to the charge transfer transition from sulphur to molyb-

Table 2. UV–Vis spectral^a and cyclic voltammetric data.^a

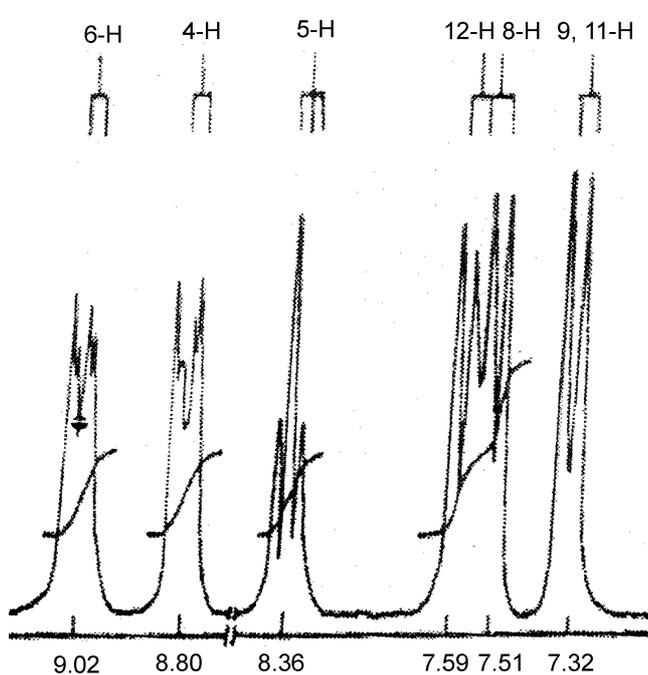
Complexes	I_{\max} (nm) ($10^{-3} e (M^{-1} cm^{-1})$)	Ru ^{III} –Ru ^{II} couple $E_{1/2}^1$ (ΔE)	Mo ^{IV} –Mo ^V couple $E_{1/2}^2$	Ligand reduction $-E_{1/2}^3$ (ΔE)	(ΔE^0) (V)
2a	569(5.94), 512(5.24) ^s , 374(21.88)	1.30(100)	1.70	0.50(100), 0.92(110), 1.65(120)	1.80
2b	560(5.01), 510(5.0) ^s , 375(20.11)	1.20(90)	1.67	0.59(110), 0.99(110), 1.75(100)	1.79
2c	566(5.68), 506(4.99) ^s , 380(21.11)	1.38(90)	1.71	0.45(90), 0.82(100), 1.45(120)	1.83
2d	573(4.98), 508(4.76) ^s , 378(20.22)	1.18(100)	1.69	0.60(100), 1.02(90), 1.80(110)	1.78
2e	562(4.97), 502(4.76) ^s , 379(20.01)	1.16(90)	1.67	0.63(100), 1.12(90), 1.85(120)	1.79

^aSolvent: CH₂Cl₂; ^sshoulder; supporting electrolyte [nBu₄N][ClO₄] (0.1 mol), working electrode: Pt-disk micro-electrode; auxiliary: Pt-wire, reference electrode: SCE, potential $E_{1/2} = 0.5 (E_{pa} + E_{pc})$ in V, peak-to-peak separation ΔE ($= |E_{pa} - E_{pc}|$) in mV, E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential

Table 3. ¹H-NMR spectral data, d (J/Hz), ppm of the complexes in DMSO-*d*⁶.

Compd.	4-H ^a	5-H ^b	6-H ^c	8-H ^a	9-H ^b	10-H ^c	11-H ^b	12-H ^a	Ar-Me ^d
2a	9.06 (9.0)	7.85 (7.5)	9.88 (9.0)	7.66 (7.5)	7.18 (7.5)	7.39	7.15 (7.5)	7.82 (7.5)	
2b	8.97 (8.1)	7.75 (8.1)	9.75 (9.0)	7.6 (8.4)	6.82 (8.4)	–	6.82 (8.4)	7.77 (8.4)	2.53
2c	9.08 (8.4)	7.88 (8.4)	9.9 (8.4)	7.68 (7.8)	7.21 (7.8)	–	7.21 (7.8)	7.84 (7.8)	
2d	8.79 (8.1)	7.70 (8.4)	9.71 (9.0)	7.5 (8.1)	6.72 (8.4)	–	6.74 (8.1)	7.67 (8.4)	2.13 ^d
2e	9.0 (8.4)	7.90 (8.1)	9.93 (8.4)	7.78 (7.8)	7.28 (8.8)	–	7.24 (7.8)	7.89 (9.0)	

^aDoublet; ^btriplet; ^cmultiplet; ^dsinglet (OMe)

**Figure 2.** ¹H-NMR spectra of [(Maapm)₂Ru(*m*-S)₂Mo(OH)₂] (**2b**) in DMSO.

denum, since a similar strong sulphur to molybdenum charge transfer transition has been observed in the 450–500 nm range for various cluster compounds

involving the MoS₄ moiety.^{20–25} A broad high intense band near 350 nm is due to ligand centred transitions (ILCT) involving energy levels higher than that of the ligand LUMO.^{17–24}

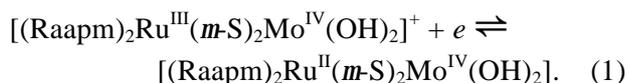
The ¹H-NMR spectral data are set out in table 3 and figure 2. Because of sufficient solubility in DMSO-*d*⁶. I collected the spectra in this medium. The assignment has been done with reference to spin–spin interaction,^{20–26} on comparing with the spectra of *ctc*-Ru(R-aapm)₂Cl₂^{13–19} and (NH₄)₂MoS₄. The downfield portion is due to the pyrimidine protons 4–6 H and the upfield signals refer to azo–aryl protons (8–12 H). The aryl protons are affected by substitution. Electron-donating –Me, –OMe group shift the aryl protons upfield, while electron-withdrawing –Cl, –NO₂ groups shift them downfield, compared with the phenyl group. 9 and 11 H are partly perturbed due to changes in the electronic properties of the substituents in the 10 position.²⁴ The proton's movement is corroborated with the electronic effect of the group.^{20–26}

3.3 Electrochemistry

Redox properties of the complexes have been studied by cyclic voltammetry in MeCN using a platinum disc working electrode in the presence of [n-Bu₄N]

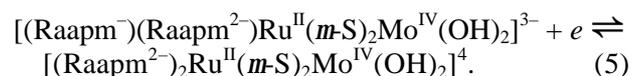
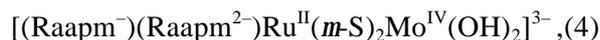
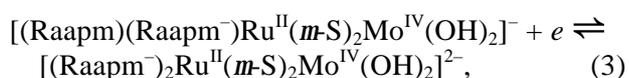
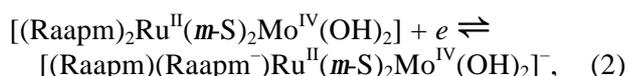
[ClO₄] as supporting electrolyte. The redox data are summarized in table 2 and a representative voltammogram is shown in figure 3 with all metal oxidation and ligand reduction parts.

A quasireversible voltammogram is observed at 1.10–1.4 V (couple II) and is referred to the Ru(III)/Ru(II) redox couple. The quasireversibility is defined from peak-to-pick separation, $\Delta E_p > 110$ mV. The formal potential of the couple, (1), varies depending on the nature of the R group present in the ligand, as expected.^{24–26}



The complexes (**2a–2e**), exhibit a second irreversible oxidation process near 1.7 V (couple II). This irreversible oxidation could be due to either the Ru(III)/Ru(IV) redox couple or the Mo(IV)/Mo(V) redox couple. Here the potential difference between the two successive oxidation processes is ≈ 0.4 V. The average potential difference between the two successive redox processes of the ruthenium centre in mononuclear complexes having C, N, O, S donor centres have been observed, in many cases, to be in the 1.3–1.5 V range.^{24–26} Therefore it seems reasonable to consider this irreversible response as due to oxidation of the Mo^{IV}–Mo^V centre.

The couples appear to be negative to SCE and are referred to the reduction of coordinated ligands. Two consecutive reductions at –0.37 to –0.67 and –0.82 to –1.12 V are due to azo/azo[–] couples. The LUMO of arylazopyrimidine is dominated by the azo function and thus the reduction is assigned to electron addition to the azo group. Thus four reductive couples refer to reduction of two-coordinated azo groups present in complexes (**2a–2e**). Instead of observing all four ligand-based reductions separately, the first two reductions (2) and (3) appear to be distinct (couple III, IV), the other reductions (4) and (5) being overlapping (couple V). So the third couple is observed at > -1.4 V and is assigned to the reduction of coordinated azo:



4. Conclusion

In the present study, the *ctc*-[Ru(R-aapm)₂(EtOH)₂](ClO₄)₂ complexes is treated with (NH₄)₂MoS₄ to synthesise [(R-aapm)₂Ru(m-S)₂Mo(OH)₂]. The formation of the Ru(m-S)₂Mo linkage stabilizes the RuL₂ fragment of (**2a–2e**) complexes preferentially in the *trans-cis* configuration. The complexes have been characterized by IR, UV–Vis and ¹H-NMR spectral data. The microanalytical and conductance data also support the composition of the complexes. The complexes show reversible Ru(III)/Ru(II) metal oxidation and four successive ligand reductions.

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References

1. Bowmarker G A, Boyd P W D, Sorrensen R J, Read C A and McDonald S W 1985 *Inorg. Chem.* **24** 3
2. Callahan K P and Piliero P A 1980 *Inorg. Chem.* **19** 2619, and references therein
3. Coucovanis D and Hadjikyriacou A 1987 *Inorg. Chem.* **26** 1
4. Stremple P, Baenziger N C and Coucovanis D 1981 *J. Am. Chem. Soc.* **103** 4601
5. Pouchert J (ed.) 1993 *The Aldrich library of NMR spectra* (Aldrich Chem Co Inc) vol 2; Cotton F A and Wilkinson G 1994 *Advanced inorganic chemistry*, 5th edn (Wiley-Interscience) p 338; Greenwood N N and Earnshaw A 1989 *Chemistry of the elements* (Oxford: Pergamon) p 519
6. Grover N, Gupta N and Thorp H H 1932 *J. Am. Chem. Soc.* **114** 3390
7. van Vliet P M, Haasnoot J G and Reedijk J 1994 *Inorg. Chem.* **33** 1934
8. Misra T K, Das D, Sinha C, Ghosh P K and Pal C K 1998 *Inorg. Chem.* **37** 1672
9. Misra T K and Sinha C 1999 *Indian J. Chem.* **A38** 346; Misra T K and Sinha C 1999 *Transition Met. Chem.* **24** 172
10. Pal S, Misra T K, Sinha C, Slawin A M Z and Woolins J D 2000 *Polyhedron* **19** 1925
11. Byabartta P, Dinda J, Santra P K, Sinha C, Panneerselvam K, Liao F-L and Lu T-H 2001 *J. Chem. Soc., Dalton Trans.* 2825

12. Byabartta P, Jasimuddin Sk, Ghosh B K, Sinha C, Slawin A M Z and Woollins J D 2002 *New J. Chem.* **26** 1415
13. Byabartta P, Santra P K, Misra T K, Sinha C and Kennard C H L 2001 *Polyhedron* **20** 905
14. Byabartta P, Pal S, Misra T K, Sinha C, Liao F L, Panneerselvam K and Lu T-H 2002 *J. Coord. Chem.* **55** 479
15. Byabartta P, Pal S, Ray U and Sinha C 2001 *Indian J. Chem.* **A40** 896
16. Byabartta P, Jasimuddin Sk, Mostafa G, Lu T-H and Sinha C 2003 *Polyhedron* **22** 849
17. Santra P K, Byabartta P, Chattopadhyay S, Falvello L R and Sinha C 2002 *Eur. J. Inorg. Chem.* 1124
18. Jasimuddin Sk, Byabartta P, Mostafa G, Lu T-H and Sinha C 2004 *Inorg. Chim. Acta* **357** 2015
19. Jasimuddin Sk, Byabartta P, Mostafa G, Liou J-C, Lu T-H and Sinha C 2004 *J. Coord. Chem.* **57** 75
20. Chakravarty A R and Chakravorty A 1983 *J. Chem. Soc., Dalton Trans.* 961
21. Constable E C 1989 *Coord. Chem. Rev.* **93** 205; Bottomley F and Mukaida M 1982 *J. Chem. Soc., Dalton Trans.* 1933
22. Das D 1998 Ph.D. thesis, Burdwan University, Burdwan; Saha A, Das C, Goswami S and Peng S-M 2001 *Indian J. Chem.* **A40** 198; Seal A and Ray S 1984 *Acta Crystallogr.* **C40** 929
23. Mondal B, Paul H, Puranik V G and Lahiri G K 2001 *J. Chem. Soc., Dalton Trans.* 481
24. Samanta R, Munsri P, Santra B K and Lahiri G K 1999 *Polyhedron* **19** 995; Srinivasan B R and Sarkar S 1990 *Inorg. Chem.* **29** 3898
25. Chattopadhyay S, Ghosh K, Pattanayak S and Chakravorty A 2001 *J. Chem. Soc., Dalton Trans.* 1259
26. Ghosh P, Pramanik A, Bag N, Lahiri G K and Chakravorty A 1993 *J. Organomet. Chem.* **454** 237