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Ruthenium azo complexes: Synthesis, spectra and electrochemistry of dithiocyanato-bis-{1-(alkyl)-2-(arylazo)imidazole}ruthenium(II)

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ABSTRACT

Silver assisted aquation of blue cis-trans-cis-RuCl2 (RaaiR´)2 (1) leads to the synthesis of solvento species, blue-violet cis-trans-cis-[Ru(OH2)2(RaaiR´)2](ClO4)2 [RaaiR = p-R-C6H4-N=N-C3H2-NN, (2), abbreviated as N,N/-chelator, where N(imidazole) and N(azo) represent N and N/, respectively; R = H (a), p-Me (b), p-Cl (c) that have been reacted with NCS− in warm EtOH resulting in red-violet dithiocyanato complexes of the type, [Ru(NCS)2(RaaR)2] (3-5). The solution structure and stereoretentive transformation in each step have been established from 1H n.m.r. results. All the complexes exhibit strong MLCT transitions in the visible region. They are redox active and display one metal-centred oxidation and successive ligand-based reductions. Linkage isomerisation was studied by changing the solvent and then UV-Vis spectral analysis.

Keywords: 1-alkyl-2-(arylazo)imidazole, thiocyanato, ruthenium(II), MLCT, NMR, CV, IR.

1. INTRODUCTION

The nature of chemical reactions of organic substrates can vastly be affected by their coordination to metal ions. It is now known that organonitriles are activated by metal coordination toward addition reactions leading to a variety of synthetic transformations of RCN species. Thiocyanates, as ligand, have attracted considerable attention in recent years not only because of their versatile coordination abilities but also some of their transition metal complexes have been found to be useful. The ruthenium chemistry of diimine ligands is an area of significant current interest, particularly with regard to the photophysical and photo-chemical properties exhibited by such complexes. Di-imine ligands are strong π-acceptors and are recognized stabilizers of the +2 state of ruthenium (low-spin d6, S=0). As a consequence, an interesting aspect of the ruthenium–diimine chemistry has been to study the remarkable π-interaction between the filled t2 orbitals of ruthenium(II) and the low-lying vacant π*-orbital of the diimine chromophore. The extent of π-interaction in these complexes depends primarily on the nature of the diimine ligands, which again depends on the nature of the groups linked to the two carbons and the two imine-nitrogens. The presence of other π-acceptor ligands within the coordination sphere may also have significant influence on the π-interaction between the diimine ligands and ruthenium(II)[1-5]. From the viewpoint of the principle of hard and soft acids and bases, both the RuNCS and RuSCN isomers can occur in the ruthenium complexes. For the last few years, the search for a suitable precursor to synthesize NCS complexes is a challenging domain and the compounds are found to be useful in this context[6-11]. Recently, we have developed the arylazopyrimidine as well as arylazoimidazole chemistry of ruthenium(II) and have synthesised dichloro componds and diaquo species. Syntheses of hetero-tris-chelates, [Ru(bpy)n(RaaiR/)3-n](ClO4)2 [bpy = 2,2′-bipyridine; n = 1, n = 2) from the solvento complexes [Ru(OH2)2(bpy)2]2+/[Ru(OH2)2(RaaiR/)2]2+ containing labile reaction centres are reported from Prof. Sinha´s laboratory[12-23]. In this paper, I examine the reaction of NCS− towards [Ru(OH2)2(RaaiR)2]2+ and the reactions of the complexes derived there-from and also studied the dinuclear adduct formation pathway. The complexes were well charecterised by C.H.N, FT-I.R, U.V-Vis, and Cyclic Voltammetrically. Linkage isomerisation was studied by changing the solvent and then UV-Vis spectral analysis.

2. EXPERIMENTAL

Published methods were used to prepare RaaiR[7-8], ctc-RuCl2 (RaaiR)2[7-8], ctc-[Ru(OH2)2(RaaiR)2](ClO4)2 . All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, India). The purification of MeCN and preparation of [n-Bu4N][ClO4] respectively used as solvent and supporting electrolyte in electrochemical experiments were done following the literature method. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. Solution electronic spectra were recorded on a JASCO UV-VIS-NIR V-570 spectrophotometer. I.r. spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000-200 cm-1). The 1H nmr spectra in CDCl3 were obtained on a Bruker 500 MHz FT n.m.r spectrometer using SiMe4 as internal reference. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10-3 M in acetonitrile. Electrochemical work was carried out using an EG & G PARC Versastat computer controlled 250 electrochemical system. All experiments were performed under a N2 atmosphere at 298K using a Pt-disk milli working electrode at a scan rate of 50 mVs-1. All results were referenced to a saturated calomel electrode (SCE). Reported potentials are uncorrected for the junction effect.

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Preparation of cis, trans, cis-Dithiocyanato-bis-{1-methyl-2-(p-tolylazoimidazolee} ruthenium(II), ctc-Ru(NCS)2 (MeaaiMe)2

CAUTION ! Perchlorates of heavy metal ions with organic ligands are potentially explosive. The syntheses involve in some cases the use of perchlorate ions. Three independent methods were employed to synthesise.

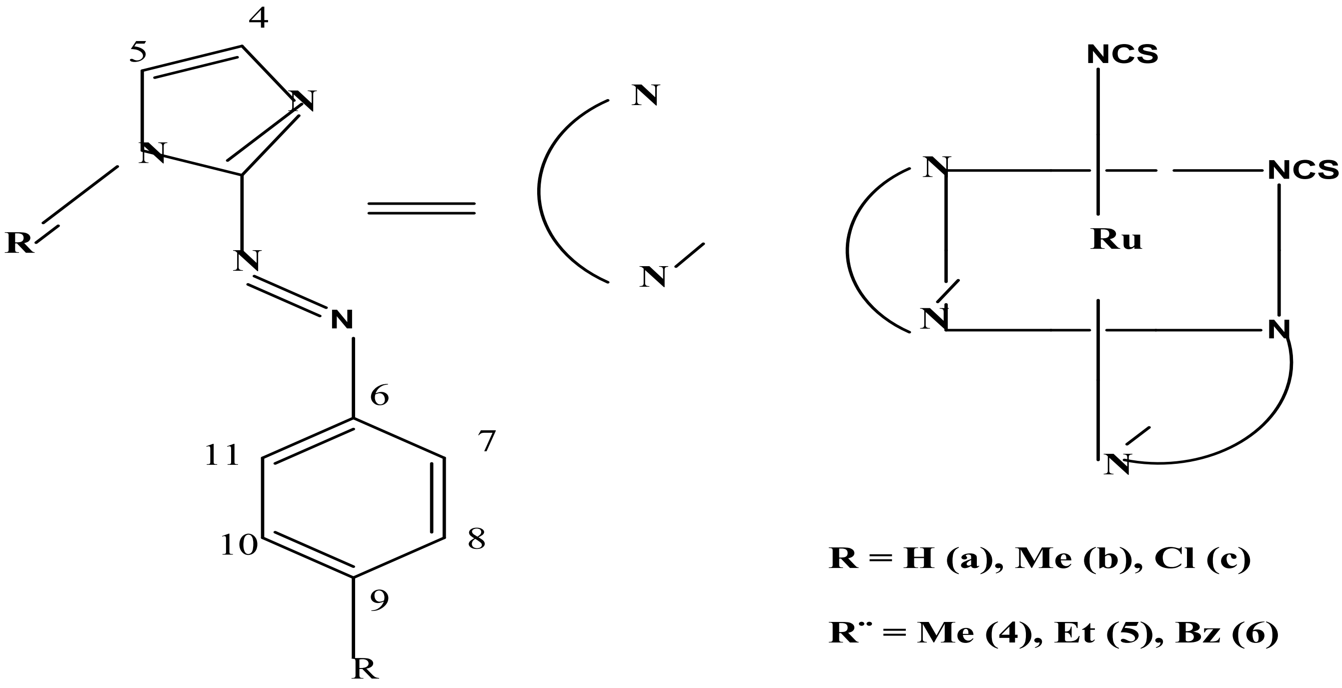
Method (a). To an EtOH blue-violet solution (15 cm3) of ctc-[Ru(OH2)2(MeaaiMe)2](ClO4)2 (0.1 g, 0.14 mmol) was added 0.019 g (0.27 mmol) of solid NH4NCS, and the mixture was stirred at 343-353 K for 12 h. The violet solution that resulted was concentrated (4 cm3) and kept in a refrigerator overnight (12 h). The precipitate was collected by filtration, washed thoroughly with H2O and dried in vacuo over CaCl2. Analytically pure (7b) was obtained after chromatography over an alumina (neutral) column on eluting the red-violet band with toluene-acetonitrile (4:1, v/v) and evaporating slowly in air. The yield was 0.088 g (80%).

Method (b). To a suspension of ctc-RuCl2(MeaaiMe)2 (4b) (0.1 g, 0.18 mmol) in EtOH (25 cm3) was added an aqueous solution of AgNO3 and stirred at room temperature (300 K) for 2 h. The AgCl which precipitated was filtered through a G-4 sintered crucible. An EtOH solution of NH4NCS (0.025 g, 0.35 mmol) was added to the filtrate, and the resulting mixture was stirred at room temperature for 8 h under a N2 atmosphere. The violet solution was concentrated by slow evaporation and the precipitate was processed as in Method (a); yield, 0.047 g (45%).

Method (c). To a CH2Cl2-Me2CO (1:1, v/v, 30 cm3) solution of ctc-RuCl2(MeaaiMe)2 (4b) (0.1 g, 0.18 mmol) was added an H2O-Me2CO solution of NH4NCS (0.024 g, 0.35 mmol). The mixture was stirred at 343-353 K for 30 h. The resulting violet solution was processed as in method (a) to give analytically pure dithiocyanato complexes; yield, 0.021 g (20%). The high yield in method (a) has prompted us to follow this route for the syntheses of the other complexes (3b-3e). The yields varied in the range 65-85%.

3. RESULTS AND DISCUSSION

Diaquo complexes ctc-[Ru(OH2)2(RaaiR)2](ClO4)2, prepared by Ag+-assisted aquation of ctc-RuCl2(RaaiR)2 , were reacted with NH4NCS (excess amount >3 mol) under stirring at 343-353 K in aqueous alcohol to give Ru(NCS)2(RaaiR)2 (3-5) in good yield (65-85%). The synthetic routes are shown in Scheme 1. The dithiocyanato were synthesized in low yield either directly on stirring in ethanol-acetone mixture for 30 h or in situ synthesis of the aquo complex by AgNO3 followed by the reaction with NH4NCS. The composition of the complexes is supported by microanalytical results. Room temperature solid state magnetic susceptibility measurements show that the complexes are diamagnetic (t2g6, S = 0). The violet dithicyanato complexes are soluble in common organic solvents but insoluble in H2O. In MeCN, they show as non-electrolytic behaviour is found for type complexes as indicated by their very low ΛM values (10-20 Ω-1cm-1mol-1).



R = H (a), Me (b), Cl (c)

R¨ = Me (4), Et (5), Bz (6)

I.r. spectra of the complexes, Ru(NCS)2(RaaiR)2 (3-5) show a 1:1 correspondence to the spectra of the dichloro analogue, ctc-RuCl2(RaaiR)2 except the appearance of intense stretching at 1300-1335 and 1250-1280 cm-1 with concomitant loss of ν(Ru-Cl) at 320-340 cm-1. They are assigned to ν(NCS)as and ν(NCS)s, respectively [5,6,15]. The ν(N=N) and ν(C=N) appear at 1365-1380 and 1570-1600 cm-1, respectively. The present series of Ru-NO complexes are assumed to contain linear NCS group. Other important frequencies are ν(H2O) at 3350-3400 cm-1 The solution electronic spectra of these new complexes were recorded in dry acetonitrile. Dithiocyanato complexes (3-5) exhibit multiple transitions in the uv-visible region (Table 1, Figure 1). They display intense MLCT transition in the 550-560 nm range. The transitions are blue shifted by ~ 40 nm as compared with corresponding dichloro derivatives, RuCl2(RaaiR)2 [6,8,11]. The 1H n.m.r. spectra of Ru(NCS)2(RaaiR)2 (3-5) complexes were unambiguously assigned (Table 2) on comparing with RuCl2(RaaiR)2 [7-9].

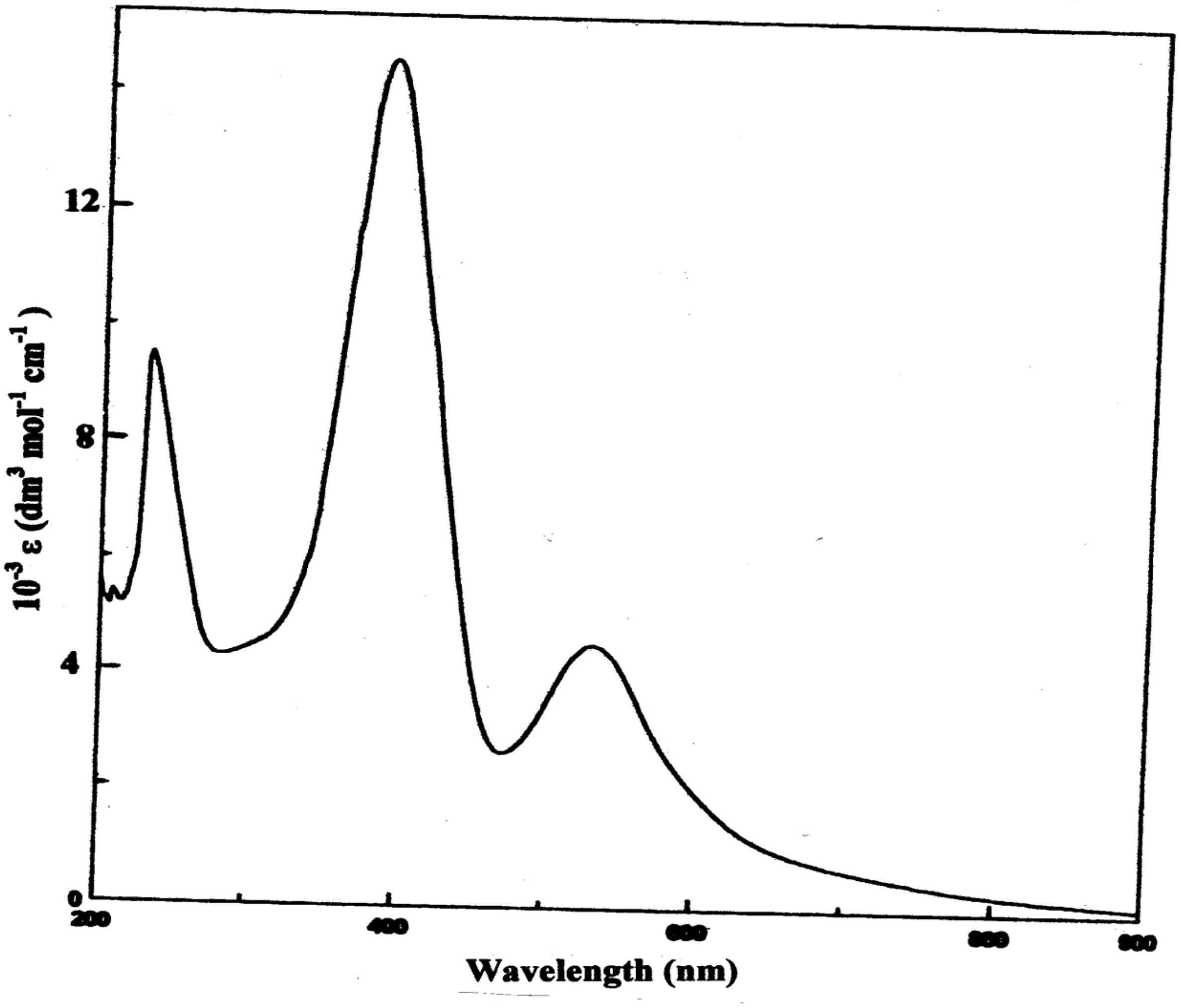


Fig-1: Complete UV-Vis spectra of the complex Ru(NCS)$_2$ (p-Me-aaiBz)$_2$, 5b

Table-1: Microanalytical (C.H.N) [a] and FT-IR spectroscopic [b] data

Complexes	C H N	ν(N=N)ν(C=N)ν(C=C)ν(NCS)
Ru(NCS)$_2$ (H-aaiMe)$_2$,**3a**	42.4 3.5 24.8 (42.3) (3.4) (24.7)	1365 1570 1600 1300 2100
Ru(NCS)$_2$ (p-Me-aaiMe)$_{2,}$ **3b**	44.4 4.0 23.6 (44.5) (4.1) (23.7)	1367 1580 1602 1320 2110
Ru(NCS)$_2$ (p-Cl-aaiMe)$_2$, **3c**	37.8 2.84 22.1 (37.7) (2.7) (22.0)	1370 1590 1610 1325 2120
Ru(NCS)$_2$ (H-aaiEt)$_2$, 4a	44.3 4.2 23.5 (44.5) (4.1) (23.7)	1375 1585 1613 1320 2105
Ru(NCS)$_2$ (p-Me-aaiEt)$_2$, 4b	37.8 4.84 22.1 (37.7) (2.7) (22.0)	1380 1590 1609 1310 2109
[Ru(NCS)$_2$(p-Cl-aaiEt)$_2$], **4c**	34.1 4.3 19.9 (34.0) (2.4) (19.8)	1370 1570 1609 1300 2108
Ru(NCS)$_2$ (H-aaiBz)$_2$, **5**^{a}	34.0 3.1 18.0 (34.1) (3.0) (18.1)	1365 1575 1606 1310 2122
Ru(NCS)$_2$ (p-Me-aaiBz)$_2$, **5b**	31.1 3.81 18.1 (31.2) (1.82) (18.2)	1380 1570 1609 1320 2133
Ru(NCS)$_2$ (p-Cl-aaiBz)$_2$, **5c**	34.2 3.2 18.1 (34.1) (3.0) (18.1)	1370 1575 1609 1310 2113

[a] Calculated values are in parenthesis; On KBr disk

The aryl protons (7-H—11-H) are downfield shifted by 0.1-0.7 ppm as compared to those of the parent dichloro derivatives. They are affected by substitution; 8- and 10-H are severely perturbed due to changes in the electronic properties of the substituents in the C(9) and C(10)-position. The aryl protons resonate asymmetrically indicative of a magnetically anisotropic environment even in the solution phase. The proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. Imidazole 4- and 5-H appear as doublet at the lower frequency side of the spectra (7.0-7.2 ppm for 4-H; 6.9-7.1 ppm for 5-H). The aryl-Me (R = Me) in Ru(NCS)2(MeaaiR)2 (3-5) appears as a single signal at 2.30 ppm and is in consonance with stereoretentive nucleophilic substitution during synthesis of dithiocyanato complexes from ctc-RuCl2(RaaiR)2 via aquo derivatives. Isomerisation of the ctc-isomer may lead to ccc-configuration belonging to C1-symmetry and would give two equally intense Ar-Me signals, which is however not the case here. The potential values of the complexes in dry acetonitrile solution are set out in Table 1. The dithiocyanato complexes exhibit a quasi-reversible (ΔEP ≥ 100 mV) oxidative response in the potential range 1.0-1.3 V. This is assigned to the Ru(III)/Ru(II) couple. The one-electron stoichiometry of this couple is confirmed by constant potential electrolysis vs SCE and the electron count ratio equals 0.94. The potential E1/2M is dependent on the substituent type R. The present series of complexes show higher E1/2M values than that of precursor dichloro derivatives by ~ 0.4 V. The better electron withdrawing property of NCS- over Cl- stabilises the dπ shell of the metal and thus shifts the metal-centred redox process to more anodic values. The stronger π-acidic nature of RaaiR/ compared to α-diimine system leads to better stabilisation of Ru(II) in the present series of complexes. The cyclic voltammogram of Ru(NCS)2(RaaiR/)2 exhibit some unusual behaviour on repetitive cycles. The reduction sweep shows a new wave that has a counter oxidative wave on the second sweep. The second and consecutive cycles increase the peak height with subsequent decrease of the primary couple. The assignment is based on earlier observations of similar Ru-bipyridine [21] and Ru-azopyridine [11] systems. The potential values of the present set of complexes lie between bipyridine and azopyridine analogous complexes and follow the order azopyridine > azoimidazole > bipyridine. This is in line of π-acidity order of these different ligand systems. The one-electron stoichiometry of the couples is assigned by comparison of current heights in differential pulse voltammetry experiments. Successive reductions on the negative side of SCE were observable and one-electron nature was confirmed by comparing the current heights of these process with that of couple II in the differential pulse voltammetry experiments and are assigned to the reduction of coordinated ligand. The azo group in RaaiR/ may accommodate two electrons and hence two coordinated ligands should exhibit four reductive responses. However, within the available potential window two reductions were clearly observable.

Table-2: UV-Vis[a] and cyclic voltammetric[b] data

Compound	**UV-Vis spectra λ_{max}(nm)(10^{-3} ε/dm^3 mol^{-1} cm^{-1})**	**Cyclic Voltammetric data E/V (ΔE_P / mV)**	
		E^{M1}	**$-E^{L}$**
(**3a**)	551(8.379),421(8.914)[d], 373(18. 3)	1.188(110)	0.388(80), 0.651(130)
(**3b**)	548(6.773), 421(12.271)[d], 379(17.791)	1.101(115)	0.407(95), 0.691(120)
(**3c**)	555(13.919), 424(13.416)[d], 384(40.721)	1.201(107)	0.344(80), 0.673(100)
(**4a**)	550(8.796), 416(10.081)[d], 376(20.755)	1.108(120)	0.377(80), 0.632(75)
(**4b**)	547(8.752), 423(7.149)[d], 380(23.694)	1.011(80)	0.383(85), 0.647(100)
(**4c**)	550(3.996)[d], 408(10.616), 258(12.403)	1.010(110)	0.401(80) 0.711(120)
(**5a**)	555(3.118)[d], 412(13.016), 260(14.469)[d]	1.032(120)	0.351(85), 0.621(120)
(**5b**)	550(3.996)[d], 408(10.616), 258(12.403)	1.010(110)	0.401(80), 0.711(120)
(**5c**)	555(3.118)[d], 412(13.016), 260(14.469)[d]	1.032(120)	0.351(85), 0.621(120),

[a] Solvent dry MeCN; [d] shoulder; [b] Solvent dry MeCN, supporting electrolyte [$^{n}Bu_4N$][ClO_4] (0.1M), w.e. Pt-disk, a.e. Pt-wire, r.e. SCE, solute conc. ~10^{-3} M, scan rate 50 mVs^{-1}, E^{M} : metal oxidation, eqn (3), E^{L} : ligand reductions, $\Delta E_P = | E_{pa} - E_{pc}|$ V where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential.

3.1 *Synthesis and Separation of the Linkage Isomers.*

[$RuCl_2(RaaiR)_2$] was prepared according to a previous report in the literature. The violet product of [$Ru(NCS)_2(RaaiR)_2$] was synthesized by a method as mentioned above. To a DMSO solution of [$RuCl_2(RaaiR)_2$] (0.2 mmol) was added an aqueous solution containing 2 equiv of $AgNO_3$ (0.068 g) and the reaction mixture stirred at 100 °C for 2 h. A gray precipitate of AgCl was removed by filtration. To the resulting yellow filtrate was added an aqueous solution of excess KSCN (0.104 g, 1 mmol) at ca. 5 °C resulting in the immediate formation of the grey-violet precipitate. The precipitate was filtered and repeatedly washed with water to completely remove all traces of DMSO. This process of washing is very important to avoid the conversion. The violet crystals thus obtained were confirmed to be mostly [$Ru(NCS)_2(RaaiR)_2$] on the basis of UV-Vis spectral analysis. Recrystallization of the violet product from acetone, acetone/DMSO (99/1 v/v), and DMF formed violet crystals of [$Ru(SCN)_2(RaaiR)_2$], grey-violet crystals of [$Ru(SCN)(NCS)(RaaiR)_2$], and red-violet crystals of [$Ru(NCS)_2(RaaiR)_2$], respectively. Due to the change of hard donar centre, N to soft donar centre, S, the HOMO and LUMO gap changes, which shift the MLCT band from high energy to low energy value.

Table-3: ^{1}H-n.m.r. spectral data, δ (J/Hz), ppm of the complexes in $CDCl_3$

Compd	4-H[c]	5-H[c]	7-H[c]	11-H	8-H	10-H
(3^{a})[a]	7.15 (7.5)	7.06 (7.5)	8.03 (8.1)	7.88 (8.91)	7.80 (8.1)	7.86 (6.1)
(3b)	6.98 (7.5)	6.86 (7.5)	8.17 (8.1)	8.09 (8.1)	8.04 (8.1)	8.01 (8.01)
(3c)	7.13 (8.1)	7.02 (8.1)	8.15 (7.8)	7.99 (7.0)	7.95 (7.8)	7.92 (8.8)
(4^{a})[a]	7.14 (7.5)	7.00 (7.5)	8.01 (7.8)	7.95 (7.1)	7.85 (7.8)	7.89 (7.8)
(4b)	7.02 (8.1)	6.94 (8.1)	8.11 (7.5)	8.04 (6.5)	8.04 (7.5)	8.07 (6.5)
(4c)	7.13 (8.1)	7.06 (8.1)	8.14 (7.5)	8.06 (8.5)	8.06 (7.5)	8.0 (7.7)
(5^{a})[a]	7.06 (7.8)	6.98 (7.8)	8.08 (8.1)	8.10 (8.3)	8.00 (8.1)	7.00 (8.1)
(5b)	6.97 (8.1)	6.85 (8.1)	8.21 (8.1)	7.80 (8.1)	8.10 (8.1)	8.50 (8.7)
(5c)	7.11 (7.8)	7.02 (7.8)	8.15 (8.1)	8.00 (6.1)	8.05 (8.1)	7.05 (8.01)

[a] δ(9-H) 7.60 ppm(m); [b] δ (9-Me); [c] doublet; [d] triplet; [e] N-Bz, AB type sextet, geminal coupling constant,4.98,4.78,; [f] 1-Me, singlet, 1.98; [g] N-Et, AB type quartet, geminal coupling constant, 4.44,4.12.

4. CONCLUSIONS

Dithiocyanato complexes of ruthenium(II)–azoimidazole, ctc-Ru(NCS)2(RaaiR)2 have been synthesised by stereoretentive reaction of diaquo complex [Ru(OH2)2(RaaiR)2]2+ with thiocyanate ion. The complexes exhibit strong MLCT transitions. Voltammetric study shows Ru(III)/Ru(II) couple along with successive ligand-based reductions. Linkage isomerisation was studied by changing the solvent and then UV-Vis spectral analysis.

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