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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*-$RuCl_2(RAaiR')_2$ (I) leads to the synthesis of solvento species, blue-violet *cis-trans-cis*-$[Ru(OH_2)_2(RAaiR')_2](ClO_4)_2$ (II), where RAaiR' = *p*-R–C_6H_4–N=N–C_3H_2–NN, abbreviated as N,N' chelator (N(imidazole) and N(azo) represent N and N', respectively); R = H (a), *p*-Me (b), *p*-Cl (c); R' = Me (III), Et (IV), Bz (V), that reacted with NCS^- in warm EtOH resulting in red-violet dithiocyanato complexes of the type $[Ru(NCS)_2(RAaiR)_2]$ (IIIa–Vn). These complexes were studied by elemental analysis, UV–Vis, IR, and ^1H NMR spectroscopy and cyclic voltammetry. The solution structure and stereoretentive transformation in each step have been established from ^1H NMR results. All the complexes exhibit strong MLCT transitions in the visible region. They are redox active and display one metal-centered oxidation and successive ligand-based reductions. Linkage isomerisation was studied by changing the solvent and then by UV–Vis spectral analysis.

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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 ligands have attracted considerable attention in recent years not only because of their versatile coordination abilities but also because 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 photochemical properties exhibited by such complexes. Diimine ligands are strong π-acceptors and are recognized stabilizers of the +2 state of ruthenium (low-spin d^6, $S = 0$). As a consequence, an interesting aspect of the ruthenium–diimine chemistry was to study the remarkable π-interaction between the filled t_2 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 can 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 [6–18]. Recently, we have developed the arylazopyrimidine, as well as arylazoimidazole chemistry of ruthenium(II), and have synthesized dichloro compounds and diaquo species. Syntheses of hetero-*tris*-chelates, $[Ru(Bipy)_n(RAaiR')_{3-n}](ClO_4)_2$ (Bipy = 2,2'-bipyridine; n = 1, 2) from the solvento complexes $[Ru(OH_2)_2(Bipy)_2]^{2+}/[Ru(OH_2)_2(RAaiR')_2]^{2+}$ containing labile reaction centers are reported in [19–23]. In this paper, we examine the reaction of NCS^- towards $[Ru(OH_2)_2(RAaiR)_2]^{2+}$ and the reactions of the complexes derived therefrom and also studied the dinuclear adduct formation pathway. The complexes were well characterized by C, H, N, FT-IR, UV–Vis, and cyclic voltammetry. Linkage isomerization was studied by changing the solvent and then by UV–Vis spectral analysis.

EXPERIMENTAL

Published methods were used to prepare RAaiR', *ctc*-$RuCl_2(RAaiR')_2$, and *ctc*-$[Ru(OH_2)_2(RAaiR')_2](ClO_4)_2$ [10–12]. All other chemicals and organic solvents used for preparative work were of reagent grade

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(SRL, India). The purification of MeCN and preparation of [n-Bu_4N][ClO_4], 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. IR spectra were obtained using a JASCO 420 spectrophotometer (KBr disks, 4000–200 cm^{-1}). The ^1H NMR spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT NMR spectrometer using $SiMe_4$ as internal reference. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10^{-3} mol/l in acetonitrile. Electrochemical work was carried out using an EG & G PARC Versastat computer-controlled 250 electrochemical system. All experiments were performed under an N_2 atmosphere at 298 K 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.

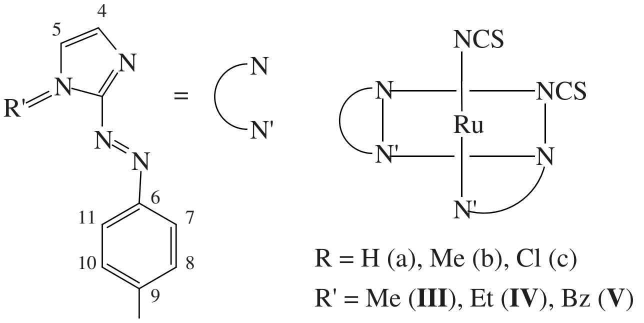
Synthesis of *cis*, *trans*, *cis*-dithiocyanato-bis-{1-methyl-2-(*p*-tolylazoimidazolee} ruthenium(II), *ctc*-$Ru(NCS)_2(MeAaiMe)_2$(IIIb). a) To an EtOH blue-violet solution (15 cm^3) of *ctc*-[$Ru(OH_2)_2(MeAaiMe)_2$]$(ClO_4)_2$ (0.1 g, 0.14 mmol) was added 0.019 g (0.27 mmol) of solid NH_4NCS, and the mixture was stirred at 343–353 K for 12 h. The violet solution that resulted was concentrated (4 cm^3) and kept in a refrigerator overnight (12 h). The precipitate was collected by filtration, washed thoroughly with H_2O and dried in vacuo over $CaCl_2$. Analytically pure product 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%).

b) To a suspension of *ctc*-$RuCl_2(MeAaiMe)_2$ (0.1 g, 0.18 mmol) in EtOH (25 cm^3) was added an aqueous solution of $AgNO_3$ and stirred at room temperature (300 K) for 2 h. The AgCl that precipitated was filtered off through a G-4 sintered crucible. An EtOH solution of NH_4NCS (0.025 g, 0.35 mmol) was added to the filtrate, and the resulting mixture was stirred at room temperature for 8 h under an N_2 atmosphere. The violet solution was concentrated by slow evaporation and the precipitate was processed as in method (a); the yield was 0.047 g (45%).

c) To a CH_2Cl_2–Me_2CO (1 : 1, v/v, 30 cm^3) solution of *ctc*-$RuCl_2(MeAaiMe)_2$ (0.1 g, 0.18 mmol) was added an H_2O–Me_2CO solution of NH_4NCS (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. The yields varied in the range 65–85%.

RESULTS AND DISCUSSION

Diaquo complexes *ctc*-[$Ru(OH_2)_2(RAaiR')_2$]$(ClO_4)_2$, prepared by Ag^+ -assisted aquation of *ctc*-$RuCl_2(RAaiR')_2$, were reacted with NH_4NCS (excess amount >3 mol) under stirring at 343–353 K in aqueous alcohol to give $Ru(NCS)_2(RAaiR')_2$ (III–V) in good yield (65–85%) (Scheme). The dithiocyanato complex 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 $AgNO_3$ followed by the reaction with NH_4NCS. The composition of the complexes is supported by microanalytical results. Room-temperature solid state magnetic susceptibility measurements show that the complexes are diamagnetic (t_{2g}^6, $S = 0$). The violet dithicyanato complexes are soluble in common organic solvents but insoluble in H_2O. In MeCN, they show non-electrolytic behavior as indicated by their very low Λ_M values (10–20 Ohm^{-1} cm^{-1} mol^{-1}). The results of elemental analyses are given in Table 1.



R = H (a), Me (b), Cl (c)
R' = Me (**III**), Et (**IV**), Bz (**V**)

Scheme.

IR spectra of the complexes $Ru(NCS)_2(RAaiR')_2$ (**III**–**V**) (Table 1) correspond to the spectra of the dichloro analogue *ctc*-$RuCl_2(RAaiR')_2$ 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_{as}(NCS) and ν_s(NCS), respectively [5, 6]. 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(H_2O) at 3350–3400 cm^{-1}. The solution electronic spectra of these new complexes were recorded in dry acetonitrile. Dithiocyanato complexes (**III**–**V**) exhibit multiple transitions in the UV–Visible region (Table 2). They display intense MLCT transition in the 550–560 nm range. The transitions are blue-shifted by ~40 nm as compared with the corresponding dichloro derivatives $RuCl_2(RAaiR')_2$ [7, 8, 11].

The ^1H NMR spectra of the $Ru(NCS)_2(RAaiR')_2$ complexes (**III**–**V**) were unambiguously assigned (Table 3) on comparing with $RuCl_2(RAaiR)_2$ [7–9]. 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

Table 1. Elemental analysis and FT-IR spectroscopic* data of complexes **III–V**

Complex	Contents (found/calcd), %			ν(N=N) ν(NCS)	ν(C=N)	ν(C=C)
	C	H	N			
Ru(NCS)$_2$(HAaiMe)$_2$ (**IIIa**)	42.4/	3.5/	24.8/	1365	1570	1600
	42.3	3.4	24.7	1300		
Ru(NCS)$_2$(*p*-MeAaiMe)$_2$ (**IIIb**)	44.4/	4.0/	23.6 /	1367	1580	1602
	44.5	4.1	23.7	1320		
Ru(NCS)$_2$(*p*-ClAaiMe)$_2$ (**IIIc**)	37.8/	2.84 /	22.1/	1370	1590	1610
	37.7	2.7	22.0	1325		
Ru(NCS)$_2$(HAaiEt)$_2$ (**IVa**)	44.3/	4.2 /	23.5/	1375	1585	1613
	44.5	4.1	23.7	1320		
Ru(NCS)$_2$(*p*-MeAaiEt)$_2$ (**IVb**)	37.8/	4.84/	22.1/	1380	1590	1609
	37.7	2.7	22.0	1310		
[Ru(NCS)$_2$(*p*-ClAaiEt)$_2$] (**IVc**)	34.1/	4.3/	19.9/	1370	1570	1609
	34.0	2.4	19.8	1300		
Ru(NCS)$_2$(HAaiBz)$_2$ (**Va**)	34.0/	3.1 /	18.0/	1365	1575	1606
	34.1	3.0	18.1	1310		
Ru(NCS)$_2$(*p*-MeAaiBz)$_2$ (**Vb**)	31.1/	3.81/	18.1 /	1380	1570	1609
	31.2	1.82	18.2	1320		
Ru(NCS)$_2$(p-ClAaiBz)$_2$ (**Vc**)	34.2 /	3.2 /	18.1 /	1370	1575	1609
	34.1	3.0	18.1	1310		

* On KBr disk.

Table 2. UV–Vis and cyclic voltammetric data

Compund	UV–Vis spectra* λ_{max}, nm ($\varepsilon \times 10^{-3}$, dm^{3}mol^{-1}cm^{-1})	Cyclic voltammetric data E, V (ΔE_P , mV)**	
		E^M	$-E^L$
(**IIIa**)	551(8.379), 421(8.914)^a, 373(18.3)	1.188 (110)	0.388 (80), 0.651 (130)
(**IIIb**)	548(6.773), 421(12.271)^a, 379(17.791)	1.101 (115)	0.407 (95), 0.691 (120)
(**IIIc**)	555(13.919), 424(13.416)^a, 384(40.721)	1.201 (107)	0.344 (80), 0.673 (100)
(**IVa**)	550(8.796), 416(10.081)^a, 376(20.755)	1.108 (120)	0.377 (80), 0.632 (75)
(**IVb**)	547(8.752), 423(7.149)^a, 380(23.694)	1.011 (80)	0.383 (85), 0.647 (100)
(**IVc**)	550(3.996)^a, 408(10.616), 258(12.403)	1.010 (110)	0.401 (80) 0.711 (120)
(**Va**)	555(3.118)^a, 412(13.016), 260(14.469)^a	1.032 (120)	0.351 (85), 0.621 (120)
(**Vb**)	550(3.996)^a, 408(10.616), 258(12.403)	1.010 (110)	0.401 (80), 0.711 (120)
(**Vc**)	555(3.118)^a, 412(13.016), 260(14.469)^a	1.032 (120)	0.351 (85), 0.621 (120)

Notes: * Solvent dry MeCN (^{a}shoulder). ** Solvent dry MeCN, supporting electrolyte [n-Bu$_4$N][ClO$_4$] (0.1 mol/l), w.e. Pt-disk, a.e. Pt-wire, r.e. SCE, solute concentration ~10^{-3} mol/l, scan rate 50 mV s^{-1}, E^M: metal oxidation, E^L: ligand reductions, $\Delta E_P = |E_{pa} - E_{pc}|$, where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential.

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')$_2$ (**III**–**V**) appears as a single signal at 2.30 ppm and is in consonance with stereoretentive nucleophilic substitution during synthesis of the dithiocyanato complexes from

Table 3. ^{1}H NMR spectral data (δ, ppm (*J*, Hz)) of the complexes in $CDCl_3$

Compound	4-H[b]	5-H[b]	7-H[b]	11-H	8-H	10-H
IIIa[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)
IIIb	6.98 (7.5)	6.86 (7.5)	8.17 (8.1)	8.09 (8.1)	8.04 (8.1)	8.01 (8.01)
IIIc	7.13 (8.1)	7.02 (8.1)	8.15 (7.8)	7.99 (7.0)	7.95 (7.8)	7.92 (8.8)
IVa[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)
IVb	7.02 (8.1)	6.94 (8.1)	8.11 (7.5)	8.04 (6.5)	8.04 (7.5)	8.07 (6.5)
IVc	7.13 (8.1)	7.06 (8.1)	8.14 (7.5)	8.06 (8.5)	8.06 (7.5)	8.0 (7.7)
Va[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)
Vb	6.97 (8.1)	6.85 (8.1)	8.21 (8.1)	7.80 (8.1)	8.10 (8.1)	8.50 (8.7)
Vc	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] doublet.

ctc-$RuCl_2(RAaiR)_2$ via aquo derivatives. Isomerization of the *ctc*-isomer can lead to *ccc*-configuration belonging to C_1 symmetry and would give two equally intense Ar–Me signals, which is, however, not the case here.

The potential values of the complexes in a dry acetonitrile solution are set out in Table 2.

The dithiocyanato complexes exhibit a quasi-reversible ($\Delta E_P \geq 100$ 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 $E^{\mathrm{M}}_{1/2}$ depends on the type of substituent R. The present series of complexes show higher $E^{\mathrm{M}}_{1/2}$ values than that of precursor dichloro derivatives by ~0.4 V. The better electron withdrawing property of NCS^- over Cl^- stabilizes the *d*π-shell of the metal and thus shifts the metal-centered redox process to more anodic values. The stronger π-acidic nature of RAaiR' compared to the α-diimine system leads to better stabilization of Ru(II) in the present series of complexes. The cyclic voltammogram of $Ru(NCS)_2(RAaiR')_2$ exhibits some unusual behavior 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 a subsequent decrease in the primary couple. The assignment is based on earlier observations of similar Ru–bipyridine [10] 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 the coordinated ligand. The azo group in RAaiR' can accommodate two electrons and, hence, two coordinated ligands should exhibit four reductive responses. However, within the available potential window two reductions were clearly observable.

Synthesis and separation of the linkage isomers were carried out the following method. Firstly, $[RuCl_2(RAaiR')_2]$ was prepared according to a previous report in the literature. Then, 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. $AgNO_3$ (0.068 g), and the reaction mixture was stirred at 100°C for 2 h. A gray precipitate of AgCl was removed by filtration. To the resulting yellow filtrate was added to aqueous solution of excess KSCN (0.104 g, 1 mmol) at ~5°C resulting in the immediate formation of the gray-violet precipitate. The precipitate was filtered off 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 $[Ru(SCN)_2(RAaiR')_2]$, gray-violet crystals of $[Ru(SCN)(NCS)(RAaiR')_2]$, and red-violet crystals of $[Ru(NCS)_2(RAaiR')_2]$, respectively. Due to the change in the hard donor center N to soft donor center S, the HOMO and LUMO gap changes, which shifts the MLCT band from the high-energy to low-energy value.

In conclusion dithiocyanato complexes of ruthenium(II)–azoimidazole *ctc*-$Ru(NCS)_2(RAaiR')_2$ have been synthesized by thestereoretentive reaction of the diaquo complex $[Ru(OH_2)_2(RAaiR')_2]^{2+}$ with the thiocyanate ion. The complexes exhibit strong MLCT transitions. Voltammetric study shows the Ru(III)/Ru(II) couple along with successive ligand-based reductions. Linkage isomerization was studied by changing the solvent and then UV–Vis byspectral analysis.

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