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Ru(II) thioether complexes with dangling pyridine ligands

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ABSTRACT

Through two different methods, new Ru(II) polypyridyl complexes were prepared in an attempt to replicate previously reported heptacoordinate Ru(II) syntheses. The tetradentate thioethers, 1,8-bis(2′-pyridyl)-3,7-dithianonane (Pdto), 1,9-bis(2′-pyridyl)-3,7-dithianonane (Pdtn), and 1,10-bis(2′-pyridyl)-3,8-dithiadecane (Pdtd), were used to form dinuclear ruthenium(II) complexes of the type $[\{Ru(L1)\}_2(\mu\text{-}Cl)_2]^{2+}$ *via* reaction with $RuCl_3{\cdot}xH_2O$. Upon reaction of the dinuclear complexes with the triimine ligand 2,6-bis(*N*′-methyl-benzimidazolyl)pyridine ($Me_2Bzimpy$), facile symmetrical bridge cleavage occurs, producing mononuclear complexes of the form $[Ru(L1)(L2)]^{2+}$, where L1 is one of the three tetradentate thioether ligands and L2 is the tridentate triimine. A second method of producing the mononuclear $[Ru(L1)(L2)]^{2+}$ complexes involves the reaction of $Ru(L2)Cl_3$ with L1 under ethanolic conditions. In such mononuclear complexes, one of the pyridine arms of the tetradentate thioether is forced to be uncoordinated, due to the firmly hexacoordinate nature of Ru(II). A similar experiment was conducted using the pentadentate thioether 1,11-bis(2′-pyridyl)-3,6-9-dithianonane (Pttu) and the diimine Phen, forming the stable hexacoordinate $[Ru(Pttu)(Phen)]^{2+}$ complex. The mononuclear complexes exhibit single-electron Ru(II) → Ru(III) oxidative response, in the range of +825 to +845 mV versus APE, involving the removal from an electron from the t_{2g} orbital set.

1. Introduction

Ruthenium(II) complexes are normally hexacoordinate [1]; the coordination number may be reduced by incorporation of steric hindrance in the ligands, as in $[RuPhos_3Cl_2]$, or by increasing the oxidation state [2]. On the other hand, two reports propose the occurrence of heptacoordinate ruthenium(II); Ghosh et al. [3] described several Ru(II) dihalide complexes using the usually pentadentate ligand, 2,6-diacetylpyridinebis(4-(*p*-tolyl)thiosemicarbazone) which they proposed bound equatorially. Murali and Palaniandavar [4] reported the mixed-ligand complexes $[Ru(Pdto)(Terpy)]^{2+}$ and $[Ru(Bbdo)(Terpy)]^{2+}$ (Pdto = 1,8-bis(2′-pyridyl)-3,6-dithiaoctane, Bbdo = 1,8-bis(2’-benzimidazolyl)-3,6-dithiaoctane, Terpy = 2,2′:6,2″-terpyridine), assigning all pyridines of the tetradentate and tridentate ligands as being coordinated on the basis of the equivalence of the Terpy terminal pyridines in 1H NMR spectroscopy and the presence of only three magnetic environments for the heteroaraomatic rings.

As part of an ongoing exploration of ruthenium heteroaromatic systems [5] and Pdto complexes [6] and transition metal complexes with dangling donor groups [7], we report similarly constituted compounds using dinuclear $[Ru(Pdtn)(\mu\text{-}Cl)]_2(ClO_4)_2$ and the Terpy analogue $Me_2Bzimpy$, as well as the pentadentate Pttu ligand (Fig. 1). We obtained the hexacoordinate $[Ru(Pdtn)(Me_2Bzimpy)]^{2+}$ and $[Ru(Pttu)(Phen)]^{2+}$ complexes, both displaying thioether-based pendant pyridines similar to that of the $[Ru(Pdto)(dpq)(Cl)]^{+}$ (dpq = dipyrido-[3,2-d:2′,3′-f]-quinoxaline)cation synthesized by Rajendiran et al. [8]. In addition, we were able to prepare the $[Ru(Pdto)(Me_2Bzimpy)]^{2+}$ and $[Ru(Pdtd)(Me_2Bzimpy)]^{2+}$ complexes.

2. Experimental

2.1. Materials and measurements

$RuCl_3{\cdot}xH_2O$ and other reagents were used as received from Sigma–Aldrich or Fisher Chemical. Pdto [9], $Me_2Bzimpy$ [10] and $Ru(Me_2Bzimpy)Cl_3$ [11] were prepared as previously described. Acetonitrile used for electrochemistry was distilled off P_4O_{10} under N_2. UV–Vis spectra were obtained with 1 cm pathlength cells using a Perkin–Elmer Lambda 35 spectrophotometer. Electrochemical studies were performed at ambient temperature (292–298 K) on

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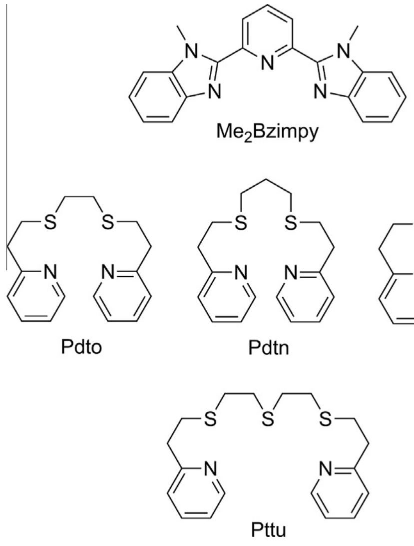

Fig. 1. Ligands used in this study.

Bioanalytical Systems BAS-100A or Epsilon System electrochemical analyzers (the latter including a BAS RDE 2 Rotator) using a three-electrode assembly consisting of a working electrode, a Pt-mesh auxiliary electrode and an Ag^+(0.01 M, 0.1 M NEt_4ClO_4, MeCN)/Ag reference electrode (APE) [12]. The working electrode was a Pt wire for voltammetry (1 mm diameter, 8.4 mm length) and a 1.6 mm diameter BAS Pt disc for rotating disc polarography. Proton NMR spectra were obtained at ambient temperature using Varian INOVA 300 MHz and 500 MHz spectrometers. Proton NMR samples were analysed in $CDCl_3$ and DMSO-d$_6$ using TMS as an internal standard. Elemental microanalyses were performed by Robertson Microlit Laboratories (Madison, NJ) and at the Pisarzhevskii Institute (Kiev, Ukraine). ESI and FAB/LSIMS mass spectrometry were performed on Thermo Finnigan TSQ70 and Micromass VG-70SE mass spectrometers, respectively, the usual matrix in the latter case being 2-nitrobenzyl alcohol. X-ray crystallography was performed at the STaRBURSTT CyberInstrumentation Consortium at Youngstown University, OH. Single-crystal XRD data for [Ru(Pttu)(Phen)]$(ClO_4)_2$·MeOH (**5**) (orange block) were collected on a Bruker AXS SMART APEX CCD diffractometer at 100(2) K using monochromatic Mo-Kα radiation, using the ω-scan technique. The unit cell was determined using SAINT+ [13], and the data were corrected for absorption using SADABS in SAINT+. The structure was solved by direct methods and refined by full-matrix least squares against F^2 with all reflections, using SHELXTL [14]. Refinement of extinction coefficients was found to be insignificant. ORTEPs shown were produced with *Mercury* 1.4.2, from The Cambridge Crystallographic Data Centre of Cambridge University. Disorder was observed for one of the perchlorate anions of [Ru(Pttu)(Phen)]$(ClO_4)_2$·EtOH and the adjacent ethanol solvate molecules. The occupancy ratio refined to 0.844(5) to 0.156(5). Atoms of the minor moiety perchlorate ion were restrained to have similar ADPs (SIMU and DELU restraints). The disordered hydroxyl O atom was restrained to have the same C–O and C···O distances as in the major moiety, and its ADP was constrained to be the same as that of its major moiety counterpart. A mild antibumping restraint was applied to keep the hydroxyl H-atom of the minor moiety from approaching other atoms.

2.1.1. [Ru(Pdtn)(μ -Cl)]$_2$(ClO$_4$)$_2$·2H$_2$O (1)

To $RuCl_3\cdot xH_2O$ (0.9 mmole, 0.23 g) in 50 mL of an 80:20 solution of ethanol/water was added 1 mmole of Pdtn (0.32 g) [15] and the mixture was refluxed for 48 h. The resultant solution was then filtered and concentrated to approximately 10 mL, followed by addition of aqueous $NaClO_4$. The resulting yellow solid was recrystallized from ethanol, to give yellow platelets in 78% yield. MS: 455 ([M$-$2ClO$_4$]$^{2+}$, 100%), 1009 ([M$-$ClO$_4$]$^+$, 1%), 1132 ([M+Na]$^+$, 1%). ^{1}H NMR (DMSO-d$_6$): δ 2.28(t, CH$_2$, J = 7.1), 2.92(m, CH$_2$, J = 7.1), 3.47(t, CH$_2$, J = 6.4), 7.08(m, pyridine, J = 5.3), 7.42(d, pyridine, J = 8.3), 7.67(t, pyridine, J = 7.5), 8.53(d, 2-pyr, J = 6.1). *Anal.* Calc. for $C_{34}H_{44}N_4Cl_2Ru_2S_4(ClO_4)_2\cdot 2H_2O$: C, 35.7; H, 4.23; N, 4.89. Found: C, 35.8; H, 3.95; N, 4.62%.

2.1.2. [Ru(Pdtn)(Me$_2$Bzimpy)](ClO$_4$)$_2$·3H$_2$O·0.5Me$_2$Bzimpy (2a)

To 1 mmol of the dinuclear complex **1** dissolved in 30 mL of ethanol was added 1.9 mmole (0.65 g) of Me$_2$Bzimpy. After the mixture was refluxed for 24 h, the solution was filtered and evaporated to approx. 10 mL. Aqueous $NaClO_4$ was then added, yielding a brown solid, which was washed with water (2 × 30 mL) and allowed to dry overnight *in vacuo*. Recrystallized from 2:1 ethanol/water. Yield: 30%. Ms: (FAB) 759 ([M$-$2ClO$_4$]$^{2+}$, 2%), 858 ([M-ClO$_4$]$^+$, 2%), 980 ([M+Na]$^+$, 1%). *Anal.* Calc. for $C_{38}H_{39}N_7RuS_2(ClO_4)_2\cdot 3H_2O\cdot 0.5$ Me$_2$Bzimpy: C, 49.3; H, 4.56; N, 11.3. Found: C, 49.5; H, 4.43; N, 11.3%.

2.1.3. [Ru(Pdtn)(Me$_2$Bzimpy)](ClO$_4$)$_2$·0.5 EtOH (2b)

Ru(Me$_2$Bzimpy)Cl$_3$ (1 mmole, 0.55 g), 1 mmole of Pdtn (1 mmole, 0.32 g) and 2 mL of triethylamine were refluxed in ethanol (50 mL) for 24 h. The resulting solution was evaporated to 15 mL and the addition of aqueous $NaClO_4$ yielded a brown solid which was washed with water (2 × 30 mL) and allowed to dry overnight *in vacuo*. Recrystallized from ethanol. Yield: 71% ms: (FAB) 858 ([M$-$2ClO$_4$+H]$^{2+}$, 81%), 980 ([M+Na]$^+$, 1%). *Anal.* Calc. for $C_{38}H_{39}N_7RuS_2(ClO_4)_2\cdot 0.5$ EtOH: C, 48.0; H, 4.71; N, 9.55. Found: C, 48.0; H, 4.52; N, 9.64%.

2.1.4. [Ru(Pdto)(Me$_2$Bzimpy)](ClO$_4$)$_2$ (3)

This complex was prepared analogously to **2b** with Ru(Me$_2$Bzimpy)Cl$_3$ (1 mmole, 0.55 g) and 1 mmole of Pdto (1 mmole, 0.30 g) as the starting materials. A brown solid precipitated was washed with water (2 × 30 mL) and allowed to dry overnight *in vacuo*. Recrystallized from ethanol. Yield: 80%. ms: (FAB) 844 ([M$-$ClO$_4$]$^+$, 37%), 745 ([M$-$2ClO$_4$]$^+$, 11%). *Anal.* Calc. for $C_{37}H_{37}N_7RuS_2(ClO_4)_2$: C, 47.1; H, 3.95; N, 10.4. Found: C, 47.0; H, 3.77; N, 10.6%.

2.1.5. [Ru(Pdtd)(Me$_2$Bzimpy)](ClO$_4$)$_2$·1.5 EtOH (4)

This complex was prepared analogously to **2b** with Ru(Me$_2$Bzimpy)Cl$_3$ (1 mmole, 0.55 g) and 1 mmole of Pdtd (1 mmole, 0.33 g) as the starting materials. A tan solid precipitated which was washed with water (2 × 30 mL) and allowed to dry overnight *in vacuo*. Recrystallized from ethanol. Yield: 65%. ms: (FAB) 872 ([M$-$ClO$_4$]$^+$, 37%).

Anal. Calc. for $C_{39}H_{41}N_7RuS_2(ClO_4)_2\cdot 1.5$ EtOH: C, 48.5; H, 4.84; N, 9.42. Found: C, 48.6; H, 4.65; N, 9.13%.

2.1.6. [Ru(Pttu)(Phen)](ClO$_4$)$_2$·EtOH (5)

(Me$_4$N)[Ru(Phen)Cl$_4$] [11] (1 mmole, 0.5 g) and Pttu [16] (1 mmole, 0.37 g) were combined and refluxed in 50 mL ethanol for 24 h. The resultant solution was filtered and evaporated to approx. 10 mL, after which an aqueous solution of $NaClO_4$ was added, producing an orange-brown solid. Recrystallization from ethanol yielded red–orange crystals, yield: 55%. ms: (FAB) 745 ([M$-$ClO$_4$]$^+$, 12%), 680 ([Ru(Pttu)(Phen)]Cl]$^+$, 15%). *Anal.* Calc. for $C_{30}H_{32}N_4RuS_3(ClO_4)_2\cdot$EtOH: C, 43.2; H, 4.30; N, 6.29. Found: C, 42.6; H, 3.91; N, 6.16%.

Caution: Perchlorate salts are potentially explosive and should be handled with care and in small quantities.