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Synthetic, spectral and structural study of mono bis(pyridine)dichloro bis(dimethyl sulfoxide-*S*) ruthenium(II) complex, $[RuCl_2(py)_2(dmso\text{-}S)_2]$ and its reactivity with nitrogen donor bases in polar and non-polar solvent

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ABSTRACT

Reaction of the *cis*-$[RuCl_2(dmso)_4]$ with pyridine (py) at room temperature in MeOH/H_2O afforded a neutral mononuclear complex *cis,cis,cis*-$[RuCl_2(py)_2(dmso\text{-}S)_2]$ **1**. The complex **1** reacted with nitrogen donor bases such as pyridine (py), pyrazine (pyz), 4,4′-bipyridine (bp) and 1,4-bis(4-pyridyl)ethane (bpeta) in different solvents to give substitution products. The nature of the substitution product was governed by the polarity of the solvents employed in the reaction. Resulting complexes have been characterized by elemental analyses, IR, NMR (^1H and ^1H–^1H COSY), ESI-MS, FAB-MS and electronic spectral studies. Molecular structures of the complexes **1** and **5** have been determined crystallographically. Complex **1** exhibits the strong intra- and inter-molecular C—H···X (X = Cl, π) and face-to-face π–π stacking interactions but only intra- and inter-molecular C—H···Cl and π–π stacking interactions are present in **5** which play important roles to stabilize crystal packing. Furthermore, the C—H···O interactions in **1** and C—H···Cl interactions in **5** lead to a single and double-helical motif.

1. Introduction

Coordination chemistry of ruthenium complexes have been studied in last few decades because of their versatile and diverse applications in various fields such as catalysis [1–3], photochemistry and photophysics [4–6] and more recently, in supramolecular [7,8] and bioinorganic chemistry [9–11].

To this end, one of the most fascinating and promising applications of ruthenium complexes are their use as chemotherapeutic agents [12]. The majority of the new drugs based on ruthenium complexes that have been prepared and tested recently (some of them already in clinical trials like NAMI-A) [13–15] are based on coordination complexes of ruthenium that contain chloro, dmso as well as a pyridine type of ligands [16–18]. Furthermore *cis*- and *trans*-$[RuCl_2(dmso)_4]$ are widely used as starting materials for the synthesis of other ruthenium complexes [19,20] through the substitution of the labile chloro and dmso groups by the desired ligands. The substitution processes are important to supramolecular chemistry because these complexes are used as building blocks to assemble complex three-dimensional architectures [21–23]. $[RuCl_2(dmso)_4]$ [24–26] as well as other Ru—Cl—dmso complexes containing other ligands, are particularly attractive as precursors [27] and catalysts for a variety of reactions such as hydrogen-atom transfer [28–30], hydrogenation [31], R-alkylation of ketones [32], aerobic oxidation of alcohols [33], oxidation of aliphatic ethers to esters [34], isomerization of alcohols [35], selective oxidation of aryl sulfides with molecular oxygen [36–38], etc. Further, metal to ligand bond strength has remarkable importance in coordination/organometallic synthetic process [39–43]. Metal–ligand link can be targeted as a strong or a weak bond. The strength of the metal–ligand link depends on the nature of the transition metal, i.e. its oxidation state and coordination number, but for a single metal targeted complex the polarity of the solvent and the availability of the counter ion in the reaction medium becomes determining factor for resulting complexes [44,45]. For neutral approaching ligands, the polar solvent facilitates the reaction by polarizing the reactant, but for a non-polar solvent such type of polarization is not possible, leading to entirely different products. During our studies directed towards synthesis and characterization of ruthenium(II) complexes, we have isolated and structurally characterized a new neutral mononuclear complex *cis,cis,cis*-$[RuCl_2(py)_2(dmso\text{-}S)_2]$ **1**. We also describe herein, the effects of polarity of the solvent on the ligand substitution reaction of **1** and molecular structure of the mononuclear complex *trans*-$[RuCl_2(py)_4]$ **5**.

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2. Experimental

2.1. Materials and physical measurements

All the synthetic manipulations were performed under ambient atmosphere. The solvents were dried and distilled before use following the standard procedures. Pyridine (S.D. Fine), pyrazine (Aldrich), 4,4′-bipyridine (Aldrich), 1,4-bis(4-pyridyl)ethane (Aldrich), Ammonium hexafluorophosphate (Aldrich) and hydrated ruthenium(III) chloride (Aldrich) were used as received. The precursor complex *cis*-[$RuCl_2$(dmso)$_4$] [19] was prepared and purified following the literature procedure.

Elemental analyses were performed on a Carlo Erba Model EA-1108 elemental analyzer and data of C, H and N is within ±0.4% of calculated values. IR(KBr) and electronic spectra were recorded using Perkin–Elmer FT-IR spectrophotometer and Shimadzu UV-1601 spectrometer, respectively. Mass spectral data were recorded using a Waters micromass LCT Mass Spectrometer/Data system. FAB mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature with m-nitrobenzyl alcohol as the matrix. The ^{1}H and ^{1}H–^{1}H COSY NMR spectra were recorded on a Bruker Spectrospin spectrometer at 300 MHz using TMS as an internal standard. The chemical shift values are recorded on the δ scale and the coupling constants (J) are in Hz.

2.2. Synthesis of complexes

2.2.1. Synthesis of complex **1**

*2.2.1.1. [$RuCl_2(py)_2$(dmso-S)$_2$] (**1**). Cis*-[$RuCl_2$(dmso)$_4$] (0.484 g, 1 mmol) was added slowly to a solution of CH_3OH (15 mL), and water (15 mL) containing pyridine (160 μL, 2 mmol). The resulting solution was stirred at room temperature for 24 h. Slowly, color of the solution changed from light yellow to dark yellow. The resulting solution was filtered and left at room temperature for slow crystallization. In a couple of days diffraction quality crystals appeared as very fine yellow shiny rods. These were separated and washed several times with diethyl ether, and vacuum-dried. Yield: (0.388 g, 80%). Anal. Calc. for $C_{14}H_{22}Cl_2N_2O_2S_2Ru$: C, 34.56; H, 4.53; N, 5.76. Found: C, 34.76; H, 4.56; N, 5.64. IR(cm^{-1}, Nujol): ν = 3443, 3103, 3005, 2924, 2675, 1631, 1486, 1447, 1351, 1302, 1224, 1158, 1088, 1020, 976, 923, 766, 701, 424. Far-IR: ν_{as} = 301, ν_s = 273, $\nu_{Ru—N(pyridine)}$ = 325 cm^{-1}. ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$, 298 K): 8.42(m, 4H, J = 5.7 Hz), 7.86(m, 4H, J = 7.5 Hz), 7.25(m, 2H, J = 8.1 Hz), 3.42(s, 12H). UV/Vis: λ_{max} ($CHCl_3$, ε [dm^3 mol^{-1} cm^{-1}]) = 399 (4781), 260 (26,808). ESI-MS (m/z): 486.4 (M^+).

2.2.2. Synthesis of neutral complexes

*2.2.2.1. [$RuCl_2(py)_2(pyz)_2$] (**2**). Cis*-[$RuCl_2$(py)$_2$(dmso-S)$_2$] (0.243 g, 0.5 mmol) was added slowly to a solution pyrazine (80 mg, 1 mmol) in toluene (15 mL). The resulting solution was refluxed with stirring at boiling temperature for 12 h. Slowly, color of the solution changed from yellow to yellowish orange. The resulting solution was filtered and left at room temperature for slow crystallization. In a couple of days yellowish orange powder was precipitated which was washed several times with diethyl ether, and vacuum-dried. Yield: (0.171 g, 70%). Anal. Calc. for $C_{18}H_{18}Cl_2N_6Ru$: C, 44.08; H, 3.67; N, 17.14. Found: C, 44.36; H, 3.76; N, 17.64. IR(cm^{-1}, Nujol): ν = 3435, 3025, 2929, 1617, 1482, 1216, 990, 806, 765, 697, 608. Far-IR: ν_{as} = 319, ν_s = 271, $\nu_{Ru—N(pyridine)}$ = 328 cm^{-1}. ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$, 298 K): 8.75(m, 8H, J = 7.0 Hz), 8.60(m, 4H, J = 6.0 Hz), 7.75(m, 4H, J = 6.0 Hz), 7.38(m, 2H, J = 6.1 Hz). UV/Vis: λ_{max} ($CHCl_3$, ε [dm^3 mol^{-1} cm^{-1}]) = 400 (23,139), 259 (35,441). ESI-MS (m/z): 492.2 (M^+).

*2.2.2.2. [$RuCl_2(py)_2(bp)_2$] (**3**). Cis*-[$RuCl_2$(py)$_2$(dmso-S)$_2$] (0.243 g, 0.5 mmol) was added slowly to a solution of 4,4′-bipyridine (156 mg, 1 mmol) in toluene (15 mL). The resulting solution was refluxed with stirring at boiling temperature for 12 h. Slowly, color of the solution changed from light yellow to dark red. The resulting solution was filtered and left at room temperature for slow crystallization. In a couple of days red crystalline powder was precipitated which was washed several times with diethyl ether, and vacuum-dried. Yield: (0.256 g, 80%). Anal. Calc. for $C_{30}H_{26}Cl_2N_6Ru$: C, 56.07; H, 4.04; N, 13.08. Found: C, 56.36; H, 4.36; N, 13.64. IR(cm^{-1}, Nujol): ν = 3429, 3025, 2910, 1593, 1480, 1406, 1213, 990, 806, 760, 690, 605. Far-IR: ν_{as} = 292, ν_s = 265, $\nu_{Ru—N(pyridine)}$ = 300 cm^{-1}. ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$, 298 K): 8.66(m, 8H, J = 6.0 Hz), 8.59(m, 4H, 7.5 Hz), 7.75(t, 2H, 6.0 Hz) 7.66(m, 8H, J = 5.1 Hz), 7.25(m, 4H, J = 8.1 Hz). UV/Vis: λ_{max} ($CHCl_3$, ε [dm^3 mol^{-1} cm^{-1}]) = 465 (3205), 258 (39,721). ESI-MS (m/z): 642.2 (M^+).

*2.2.2.3. [$RuCl_2(py)_2(bpeta)_2$] (**4**). Cis*-[$RuCl_2$(py)$_2$(dmso-S)$_2$] (0.243 g, 0.5 mmol) was added slowly to a solution of 1,4-bis(4-pyridyl)ethane (184 mg, 1 mmol) in toluene (15 mL). The resulting solution was refluxed with stirring at boiling temperature for 12 h. Slowly, color of the solution changed from light yellow to dark yellow. The resulting solution was filtered and left at room temperature for slow crystallization. In a couple of days dark yellow color powder precipitated which was washed several times with diethyl ether, and vacuum-dried. Yield: (0.226 g, 65%). Anal. Calc. for $C_{34}H_{34}N_6Cl_2Ru$: C, 58.45; H, 4.87; N, 12.03. Found: C, 58.66; H, 4.76; N, 12.20 IR(cm^{-1}, Nujol): ν = 3439, 3150, 3010, 2940, 2840, 1621, 1540, 1480, 1430, 1240, 1008, 950, 810, 750, 680. Far-IR: ν_{as} = 320, ν_s = 271, $\nu_{Ru—N(pyridine)}$ = 324 cm^{-1}. ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$, 298 K): 8.41(m, 8H, J = 6.9 Hz), 8.25(t, 4H, 5.4 Hz), 7.72(m, 4H, 7.5 Hz) 7.29(m, 8H, J = 4.5 Hz), 7.07(m, 2H, J = 6.0), 3.01(t, 4H, 12.9 Hz), 2.78(t, 4H, 4.2 Hz). UV/Vis: λ_{max} ($CHCl_3$, ε[dm^3 mol^{-1} cm^{-1}]) = 402 (4237), 261 (5709). ESI-MS (m/z): 698.8 (M^+).

*2.2.2.4. [$RuCl_2(py)_4$] (**5**). Cis*-[$RuCl_2$(py)$_2$(dmso-S)$_2$] (0.243 g, 0.5 mmol) was added a solution of toluene (15 mL) containing pyridine (80 μL, 1 mmol). The resulting solution was refluxed with stirring at boiling temperature for 12 h. Slowly, color of the solution changed from light yellow to dark red color. The resulting solution was filtered and left at room temperature for slow crystallization. In a couple of days diffraction quality crystals appeared as red blocks. These were separated and washed several times with diethyl ether, and vacuum-dried. Yield: (0.195 g, 80%). Anal. Calc. for $C_{20}H_{20}Cl_2N_4Ru$: C, 49.18; H, 4.09; N, 11.47. Found: C, 49.36; H, 4.16; N, 11.64. IR(cm^{-1}, Nujol): ν = 3440, 3106, 3005, 2924, 2674, 1630, 1540, 1488, 1447, 1250, 1006, 960, 810, 750, 688. Far-IR: ν_{as} = 300, ν_s = 271, $\nu_{Ru—N(pyridine)}$ = 326 cm^{-1}. ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$, 298 K): 7.59(m, 8H, J = 7.5 Hz), 7.40(m, 4H, J = 6.0 Hz), 7.38(m, 8H, J = 6.9 Hz). UV/Vis: λ_{max} ($CHCl_3$, ε [dm^3 mol^{-1} cm^{-1}]) = 450 (53,761), 248 (23,535). ESI-MS (m/z): 488.9 (M^+).

2.2.3. Synthesis of cationic complexes

*2.2.3.1. [$Ru(py)_2(pyz)_2$(dmso)$_2$]·(PF_6)$_2$ (**6**). Cis*-[$RuCl_2$(py)$_2$(dmso-S)$_2$] (0.243 g, 0.5 mmol) was added to a solution of CH_3OH (15 mL) and pyrazine (80 mg, 1 mmol).The resulting solution was refluxed with stirring at boiling temperature for 12 h. Slowly, color of the solution changed from yellow to red. The resulting red solution was cooled to room temperature and filtered through Celite. Ammonium hexafluorophosphate dissolved in 10 mL of methanol was added to the filtrate, whereupon a red crystalline solid separated. It was filtered and washed several times with diethyl ether. Yield: (0.266 g, 70%). Anal. Calc. for $C_{22}F_{12}H_{30}N_6O_2S_2P_2Ru$: C, 30.52; H, 3.47; N, 9.71.