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Substitution of *trans* ligands in μ-oxo-bis(μ-acetato)diruthenium(III) complexes: Synthesis and kinetic studies

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ABSTRACT

$[Ru_2O(L)_6(acetate)_2](PF_6)_2$ {L = pyridine **1**; 4-picoline **2**} undergo aquation in acetone–water (60:40 v/v) mixed solvent to form diaquo complexes in solution as shown by proton NMR studies. Ligands *trans* to the μ-oxo group are substituted. These diaquo complexes react with substituted pyridines and imidazoles to form respective disubstituted complexes. Rate constants for aquation and complexation under pseudo first order conditions of ligand are reported. Rate constants increase with increase in the basicity of incoming ligand. Disubstituted complexes proposed to be formed in solution have been isolated and characterized by elemental analyses, visible spectra, proton NMR. Single crystal X-ray structures of 4-picoline and 4-methylimidazole disubstituted complexes are reported. All the isolated complexes exhibit a strong peak between 570 and 585 nm in their visible absorption spectra. λ_{max} varies linearly with $\sum pk_a$ of terminal ligands. In disubstituted complexes of **1** with 2-methyl and 4-methyl imidazole deprotonation of N(1)H of methylimidazoles takes place in solution.

1. Introduction

The presence of oxo/hydroxo bridged bis(μ-acetato)dimetal (M = Fe, Mn) core in the active sites of natural enzymes has spurred the interest of chemists in the study of μ-oxo-bis(μ-acetato)dimetal complexes [1–7]. One such group of complexes which have particularly been studied is μ-oxo-bis(μ-acetato)diruthenium. Electrochemical, spectroscopic properties and structures of these complexes are reported [8–21]. X-ray structures of μ-oxo-bis(μ-acetato)diruthenium complexes show that the bonds *trans* to μ-oxo group are longer than those in the *cis* positions due to *trans* effect and pyridine/pyridine-d_5 exchange, and solvolysis studies indicate their lability [22–24]. However, no other data are available on this aspect. Lack of data on substitution kinetics of *trans* ligands, our interest in the solution chemistry of these complexes [20,21], and the opportunity provided by the stability of μ-oxo-bis(μ-acetato)diruthenium core in the presence of monodentate and bidentate terminal ligands lead us to investigate this aspect. In this paper, results of our studies on kinetics of substitution of *trans* ligands are reported. Complexes proposed to be formed during kinetic runs have been isolated and characterized by CHN, proton NMR and single crystal X-ray data. We were also interested to know if the methodology followed for studying kinetics could also be used as a method to synthesize *trans* disubstituted μ-oxo-bis(μ-acetato)diruthenium complexes.

2. Experimental

2.1. Materials

$RuCl_3 \cdot nH_2O$ was purchased from Johnson Matthey. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Iolar-2 grade argon (4 ppm O_2) and nitrogen (5 ppm O_2) were purchased from Indian Oxygen, Mumbai, India. Argon and nitrogen were bubbled through vanadyl sulphate and freshly prepared alkaline pyrogallate solutions, dried over ascarite and presaturated with the corresponding solvent prior to use. The organic solvents and ligands used were A.R. Grade and were purified by the reported procedure [25]. All other reagents and chemicals (A.R. Grade) were used as received. Tetrabutylammonium hydroxide solution was standardized against the standard HCl [25].

2.2. Physical measurements

Where necessary all the manipulations were done using standard Schlenk techniques.

NMR spectra were recorded on Bruker Avance DPX 200 spectrometer. In case of experiments carried out in the presence of

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DCl the complex was weighed out in the NMR tube. After dissolving the complex in the known amount of solvent, sufficient volume of 0.10M DCl was added so that the final concentration of DCl was a little less than two equivalents with respect to complex.

A Shimadzu Model PC3101 spectrophotometer equipped with temperature controller TCC 240 and provision for maintaining inert atmosphere inside the cell compartment was used to record absorption spectra and carrying out spectrophotometric experiments. Five millimetres matched cuvettes fitted with SubaSeal septa were used to measure the absorbance and record spectra. All the measurements were made at 25 °C and μ = 0.10 M (tetraethylammonium perchlorate).

pH was determined using Orion 720APlus pH meter equipped with combined glass electrode. Electrode was calibrated first with aqueous 0.05 M potassium hydrogen phthalate and then with 0.05 M potassium hydrogen phthalate in acetonitrile–water (80:20 v/v) [26]. Linearity of calibration in an aqueous solution was checked with 0.05 M disodium tetraborate solution (pH 9.18) and a mixture of 0.01 M potassium dihydrogen phosphate + 0.01 M disodium hydrogen phosphate (pH 6.85).

2.3. Single crystal X-ray diffraction studies

The structural determination was made for complexes **1a** and **1e** (see Section 2.5) which were crystallized from acetonitrile/water to give a single crystal of an appropriate size for analyses. Crystal was mounted on a glass fibre. Data for complexes **1a** and **1e** were collected using Mo Kα (λ = 0.7107 Å) radiation on a SMART APEX diffractometer equipped with CCD array detector. Crystal was selected from the mother liquor and immersed in Partone Oil and then mounted. Data collection, data reduction, structure solution/refinement were carried out using the software package (SAINT/SHELXTL/XPREP) of SMART APEX. Graphics were generated using PLATON and MERCURY 1.3.

All the structures were solved by direct methods and were refined in a routine manner. All the non-hydrogen atoms were treated anisotropically. All the hydrogen atoms are geometrically fixed at their idealized position. The crystallographic parameters are listed in Table 1. In complex **1a**, carbon atom (C-5) of 4-picoline was found to be disordered and was refined isotropically. On the other hand, in complex **1e**, the carbon atoms of the pyridine moiety (C9A and C10A) were found to be disordered and were refined using FVAR facility. One of the PF_6^- moieties was disordered around a center of symmetry. The SOF of the peaks have been refined keeping the *x*, *y*, *z* and temperature factors fixed (at 0.05). After refinement, the refined SOF of the disordered phosphorous and fluorine atoms were fixed and *x*, *y*, *z* and isotropic temperature parameters were refined in the subsequent cycle of refinements.

Table 1
Crystallographic data for complexes **1a** and **1e**

Crystal data	1a	1e
Empirical formula	$C_{36}H_{40}F_{12}N_6OP_2Ru_2$	$C_{32}H_{38}F_{10}N_8O_5P_2Ru_2$
Formula weight	1128.82	1068.78
Crystal size (mm)	0.18 × 0.06 × 0.02	0.20 × 0.08 × 0.03
Crystal system	monoclinic	orthorhombic
Space group	*C*2/*c*	$C222_1$
a (Å)	16.824(4)	14.3307(9)
b (Å)	19.945(5)	20.4882(13)
c (Å)	14.738(4)	14.1020(10)
β (^{0})	121.067(4)	
Volume (Å^3)	4236.1(19)	4140.5(5)
Z	4	4
D_{calc} (g/cm^3)	1.770	1.715
F(000)	2256	2136
μ Mo Kα (mm^{-1})	0.891	0.901
Temperature (K)	100(2)	150(2)
θ Minimum/maximum	1.74/25.05	1.73/25.49
Reflections collected/unique/observed	10075/3757/2602	10812/3858/3320
Data/restraints/parameters	3757/0/284	3858/9/270
Goodness of fit on F^2	1.106	1.002
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0597, wR_2 = 0.1147	R_1 = 0.0617, wR_2 = 0.1535
R indices (all data)	R_1 = 0.0962, wR_2 = 0.1256	R_1 = 0.0734, wR_2 = 0.1636

2.4. Synthesis of complex $[Ru_2O(L)_6(acetate)_2](PF_6)_2$ {L = pyridine **1**; 4-picoline **2**; 1-methylimidazole **3**}

Complexes **1**–**3** were synthesized by a known procedure [8]. $RuCl_3$ (0.5 g) was dissolved in mixture of water (60 ml), glacial acetic acid (40 ml) and ethanol (20 ml) and warmed to 70 °C for 10 min till the solution turned reddish. One millilitre of respective ligand was then added and contents were refluxed for 1 h. After cooling, 2 g of NH_4PF_6 was added and volume of the contents was reduced to about 20 ml in a rotary evaporator. After adding 20 ml of water, the contents were left overnight in the refrigerator. Next day, a solid separated and was collected over glass frit, washed several times with water and sucked dry. Solid was dissolved in minimum amount of acetonitrile containing a few drops of respective ligand and left in the refrigerator. Fine blue coloured needles were obtained next day. These were filtered over glass frit, washed with water several times, sucked dry and left in vacuum desiccator overnight for drying. Yields were 45% for **1**, 40% for **2** and 65% for **3**. The analytical data are presented in Table 2. The reaction was also conducted with isonicotinic acid but the desired complex was not obtained.

2.5. Syntheses of complex $[Ru_2O(pyridine)_4(L)_2(acetate)_2](PF_6)_2$ {L = 4-picoline **1a**; imidazole **1b**; 1-methylimidazole **1c**; 2-methylimidazole **1d**; 4-methylimidazole **1e**;}

Complex **1** (0.10 g) was dissolved in degassed acetone–water (60:40% v/v; henceforth referred to as mixed solvent) and left under argon overnight. Next day 0.5 ml/0.05 g of appropriate ligand was added and the mixture was left under argon for 4 h. After adding 0.05 g of NH_4PF_6, the contents were left in the refrigerator. Next day, the solid separated. It was filtered through glass frit, washed several times with water and dried under vacuum. The complexes were recrystallized by dissolving in 5 ml of acetonitrile containing a few drops/few mg of the respective ligand, adding 5 ml water Contents were left in the refrigerator. Next day crystalline solid separated. It was filtered through glass frit, washed with water, sucked dry and finally dried in vacuum desiccator. Yields varied between 80% and 90%. Analytical data for above complexes are presented in Table 2.

2.6. Synthesis of complex $[Ru_2O(4\text{-picoline})_4(L)_2(acetate)_2](PF_6)_2$ {L = pyridine **2a**; 1-methylimidazole **2b**}

Complex **2** (0.10 g) was dissolved in degassed mixed solvent and left under argon overnight. Next day 0.5 ml of appropriate ligand was added and the mixture was left under argon for 4 h. After adding 0.05 g of $NH_4(PF)_6$, the contents were left in the refrigerator. Next day, the solid separated. It was filtered through glass frit, washed several times with water and dried under vacuum. Complexes were recrystallized by dissolving in 5 ml of acetonitrile containing a few drops of respective ligand. Five millilitre of water was added, and the contents were left in the refrigerator. Next day, the crystalline solid separated. It was filtered through glass frit, washed with water, sucked dry and finally dried under vacuum. The yield was 90% for **2a** and 85% for **2b**. The analytical data are presented in Table 2.