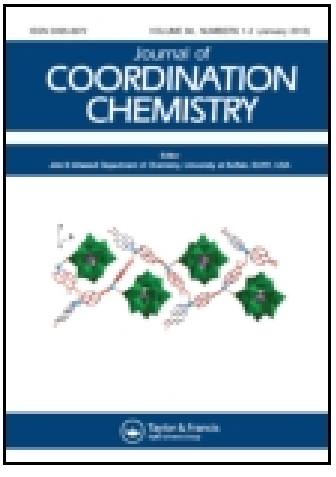

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Understanding the role of flexible 4′-functionalized polyethylene glycoxy chains on the behavior of platinum(II) (4′-(ethylene glycoxy)-2,2′:6′,2′′-terpyridine: a kinetic and a mechanistic study

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Understanding the role of flexible 4′-functionalized polyethylene glycoxy chains on the behavior of platinum(II) (4′-(ethylene glycoxy)-2,2′:6′,2″-terpyridine: a kinetic and a mechanistic study

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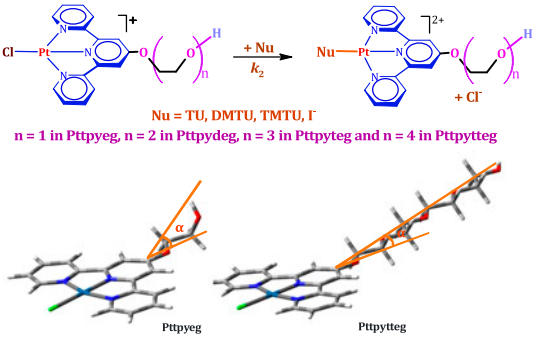

The polyethylene glycoxy pendant, *trans* to the leaving group acts as a σ-donor into the terpyridine ligand and is effective only up to $n = 1$, beyond which the substitution reactivity of the complexes are controlled by the steric influence of the appended ethylene glycoxy pendant units, which decreases with increase in the number of ethylene glycoxy units.

The ligand substitution kinetics of 4′-functionalized mononuclear Pt(II) (4′-(ethylene glycoxy)-2, 2′:6′,2″-terpyridine complexes, [Pt(nY-tpy)Cl)Cl] (where Y = ethylene glycoxy, n = number of ethylene, glycoxy units = 1, 2, 3, and 4, and tpy = 2,2′:6′,2″-terpyridine), with thiourea, 1,3-dimethyl-2-thiourea, 1,1,3,3-tetramethyl-2-thiourea, and iodide were investigated under *pseudo*-first-order conditions as a function of concentration and temperature by conventional stopped-flow technique. The observed first-order rate constants followed the simple rate law $k_{obs} = k_2[Nu]$. The data obtained show that the ethylene glycoxy pendant, *trans* to the leaving group, acts as a σ-donor into the terpyridine ligand and is effective only up to $n = 1$, beyond which the substitution reactivity of the complexes are controlled by the steric influence of the appended ethylene glycoxy pendant units, which decreases with increase in the number of ethylene glycoxy units. The activation parameters obtained support an associative mechanism, where bond formation in the transition state is favored. The observed reactivity trends were supported by density functional theory calculations.

Keywords: Substitution kinetics; Mechanistic study; Platinum

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Introduction

The tridentate N-donor ligand, 2,2′ : 6′,2″-terpyridine, also known as tpy, first reported by Burstall [1] and Morgan [1, 2], is one of the most attractive ligands for metal coordination. The ligand has very rich chemistry since it can easily form transition metal complexes with potential applications in biochemistry, photochemistry [3–6], nanoscience, and supramolecular chemistry [7–9]. In the biomedical applications, terpyridine and its derivatives are used as potential sensors for tumor cells [10] due to their ability to interact with double strand DNA and proteins [5, 11–16]. Some complexes of terpyridine were found to be cytotoxic against human ovarian cancer [12, 17]. However, interactions of some of these complexes with certain biomolecules such as sulfur donors were found to exhibit toxic side effects [18]. Therefore, the search for better cytotoxic agents with improved side effects is a focus. So there is need for investigating the mechanism of interactions of these compounds with biomolecules and DNA.

Recent synthetic techniques have opened new possibilities for the synthesis of functionalized terpyridine complexes. More importantly, functionalization in the 4′ position by using substituted terpyridine ligands such as 4′-chlorterpyridine or 4′-hydroxyterpyridine derivatives are of interest [19, 20]. However, applications of functionalized terpyridine complexes have not been fully studied.

Square-planar terpyridine derivatives are useful models for studying the substitution behavior of Pt(II) complexes [20, 21]. Only the ligand in the fourth coordination position of terpyridine is replaced in a simple substitution reaction [22]. During substitution, the π-acceptor orbitals of pyridine units in terpyridine ligand accept electrons from the metal center including those from the incoming ligand and stabilizes the transition state [23]. This π-acceptor effect is responsible for the high reactivity of the unfunctionalized Pt(II) terpyridine type complexes. Literature data focusing on understanding the substitution kinetics of unfunctionalized terpyridine complexes and its derivatives are available [20–22, 24–32].

Mononuclear Pt(II) terpyridine complexes have been useful in understanding the effect of a non-carrier ligand on the rate of substitution at the metal centers [33, 34]. It has been illustrated from previous studies that the structure and the electronic properties of the chelate ligand backbone control the rate of ligand substitution of square-planar metal complexes [21, 35–42]. Furthermore, it has also been established that the degree of lability of the leaving group is influenced by the σ- and π-structural features of the ancillary group of the terpyridine ligand system [10, 15].

The effect of the ancillary group on the π-acceptor property of the terpyridine complexes, $[Pt(R\text{-}tpy)X]^+$ (where R = H; Ph; Ph(o-CH_3); Ph(o-Cl); where Ph = phenyl group, X = Cl, OH) has been investigated previously [21, 29, 42]. Data obtained from these studies reveal that electron-withdrawing groups on the terpyridine ancillary ligand increase the rate of ligand substitution, while electron donating groups have the opposite effect. The influence of the ligand substitution is also controlled by the extent of the π-backbonding from the metal center to the terpyridine ligand backbone [21, 35–42]. Basolo *et al.* [43] and Tobe *et al.* [44] reported substitution kinetics of bis(2-pyridylmethyl)amine complexes possessing appending ancillary groups on the *trans* position of the non-labile ligand system showed that the *trans* effect was dominant over π-acceptor effect. When electron donating head groups were attached to the *trans* N, an increase in the rate of ligand substitution was observed [45]. This increase in the reactivity was thought to be due to the increased ground state stabilization caused by the *trans* effect of the appended group. Structural variations

due to such appending groups were thought to enhance the anti-tumor activity of the complex in biological systems [46].

To extend this understanding, we functionalized terpyridine at the 4′-position by polyethylene glycoxy groups. We have investigated the ligand substitution behavior of 4′-functionalized mononuclei Pt(II) terpyridine complexes of the form: [Pt(nY-tpy)Cl)Cl] (where Y = ethylene glycoxy, n = number of ethylene glycox units = 1, 2, 3, and 4, tpy = 2,2′ : 6′,2″-terpyridine) with thiourea (TU), 1,3-dimethyl-2-thiourea (DMTU), 1,1,3,3-tetramethyl-2-thiourea (TMTU), and iodide (I^-). The length of the polyethylene glycoxy tail is systematically increased by incorporating 2–4 units. It is our expectation that the results of this study will reveal the role of flexible poly glycoxy pendant groups on the substitution reactions of Pt(II) terpyridine. The structures of the investigated complexes are shown in figure 1.

Experimental

Materials

Methanol (Merck) was distilled over magnesium [47] prior to using for kinetic analysis. Dimethylsulfoxide (99.9%) from Aldrich was used without any further purification. Ethylene glycol (99.8%), diethylene glycol (99%), and triethylene glycol (99%) were bought from Sigma-Aldrich. The ligand, 4′-chloro,2,2′ : 6′,2″-terpyridine (97%), tetraethylene glycol (99%), the platinum salt, and potassium tetrachloroplatinate (II) (99.9%) were bought from Aldrich. All other chemicals were purchased from Sigma-Aldrich and used without purification.

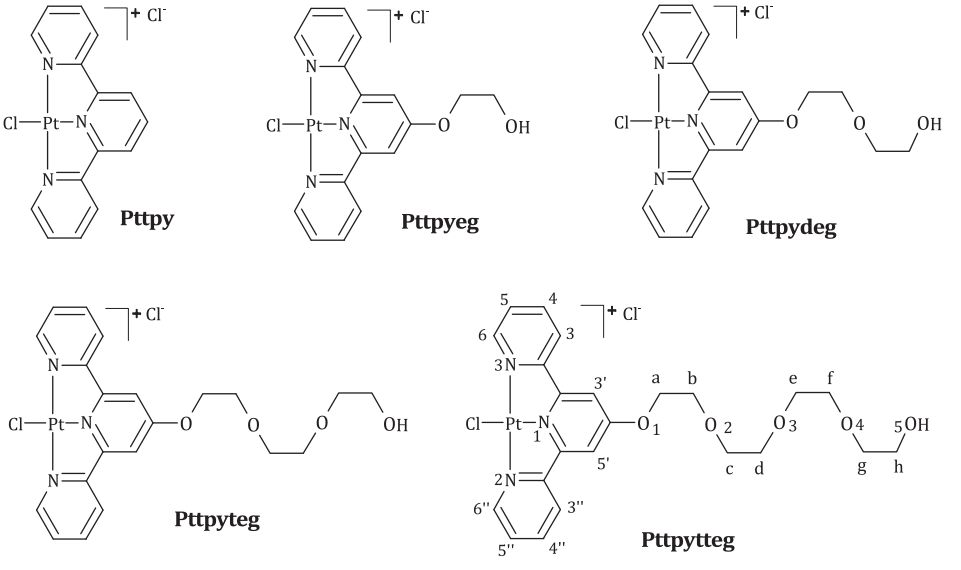


Figure 1. Structures of polyethylene glycoxy appended Pt(II) complexes studied. Shown on the diagram is the numbering scheme used. Pttpy is included for reference.

Synthesis of ligands

The syntheses of ligands were carried out by literature procedures [48–50]. To a suspension of KOH in dry DMSO at 50 °C, ethylene glycol and its respective polymer (n = 2, 3, or 4) in excess were added. After stirring for 30 min, 4′-chloro-2,2′ : 6′,2″-terpyridine was added and the reaction mixture was stirred for 20 h at this temperature. Upon cooling to room temperature, the reacting mixture was treated with deionised water and filtered. The crude product was extracted from the filtrate in dichloromethane (3 × 30 mL), dried over anhydrous magnesium sulfate, and then the solvent was removed. 4′-[2-(2-Hydroxyethoxy) ethoxy]-2,2′ : 6′,2″-terpyridine (**tpyeg**) and 4′-[2-(2-hydroxyethoxy)ethoxy]-2,2′ : 6′,2″-terpyridine (**tpydeg**) gave a white paste and a white powder, respectively. Crude products were purified in THF to give white solids. 4′-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy-2,2′ : 6′,2″-terpyridine (**tpyteg**) and 4′-{2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethoxy}-2,2′ : 6′,2″-terpyridine (**tpytteg**) yielded pale yellow oils, pure enough for platination.

The purity of the ligands was confirmed by ^{1}H NMR and mass spectroscopy. The ^{1}H NMR spectra obtained show similarity in the aromatic region for the ligands.

(tpyeg): Yield: 250 mg (70%), off white paste. ^{1}H NMR (400 MHz, $CDCl_3$)[†] δ/ppm: 8.63 (d, 2H, 6 6″), 8.55 (2H, d, 3 3″), 7.99 (2H, s, 3′ 5′), 7.79 (dt, 2H, 4 4″), 7.29 (dt, 2H, 5 5″), 4.23 (t, 2H, CH2), 3.97 (t, 2H, CH2). ^{13}C NMR (77 MHz, $CDCl_3$), δ/ppm: 61.1, 69.6, 107.6, 121.5, 123.8, 136.9, 148.9, 155.6, 157.2, 167.1. TOF MS-ES$^+$, *m/z*: 316.1062 $(M + Na)^+$.

(tpydeg): Yield: 190 mg (80%), white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.69 (d, 2H, 6 6″), 8.62 (d, 2H, 3 3″), 8.13 (s, 2H, 3′ 5′), 7.87 (t, 2H, 4 4″), 7.35 (t, 2H, 5 5″), 4.46 (t, 2H, CH2), 3.94 (t, 2H, CH2), 3.77 (t, 2H, CH2), 3.69 (t, 2H, CH2). ^{13}C NMR (77 MHz, $CDCl_3$), δ/ppm: 61.7, 68.1, 69.9, 72.8, 108.3, 121.6, 124.0, 137.1, 148.9, 155.7, 156.7, 167.3. Anal. Calcd for $C_{19}H_{19}N_3O_3$: C, 67.64; H, 5.68; N, 12.46; *Found*: C, 68.00; H, 5.81; N, 11.97. TOF MS-ES$^+$, *m/z*: 360.1324 $(M + Na)^+$.

(tpyteg): Yield: 175 mg, colorless oil (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.66 (d, 2H, 6 6″), 8.59 (d, 2H, 3 3″), 8.03 (s, 2H, 3′ 5′), 7.83 (t, 2H, 4 4″), 7.31 (t, 2H, 5 5″), 4.40 (t, 2H, CH2), 3.92 (t, 2H, CH2), 3.73 (m, 4H, CH2), 3.69 (t, 2H, CH2), 3.60 (t, 2H, CH2). ^{13}C NMR (77 MHz, $CDCl_3$), δ/ppm: 61.7, 67.9, 69.8, 70.4, 71.0, 72.9, 107.8, 121.4, 123.9, 136.9, 148.9, 155.9, 157.0, 167.1. TOF MS-ES$^+$, *m/z*: 404.1580 $(M + Na)^+$.

(tpytteg): Yield: 183 mg (74%), pale brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.38 (d, 2H, 6 6″), 8.30 (d, 2H, 3 3″), 7.72 (s, 2H, 3′ 5′), 7.58 (t, 2H, 4 4″), 7.07 (t, 2H, 5 5″), 4.11 (t, 2H, CH2), 3.63 (t, 2H, CH2), 3.44 (t, 2H, CH2), 3.37 (m, 6H, CH2), 3.27 (m, 4H, CH2). ^{13}C NMR (77 MHz, $CDCl_3$), δ/ppm: 39.5, 40.6, 42.4, 60.9, 60.9, 67.5, 69.1, 69.8, 70.0, 70.2, 70.3, 70.5, 72.5, 72.5, 107.2, 121.1, 123.8, 136.8, 148.8, 155.4, 156.7, 166.7. TOF MS-ES+, *m/z*: 448.1848 $(M + Na)^+$.

Synthesis of platinum(II) complexes

The synthesis of the complexes was carried out using the following procedure: To a stirred solution of [Pt(cod)Cl_2] [42] in dry methanol at room temperature, a suspension of the ligand in dry methanol was added at 55 °C. The reaction mixture was stirred for 24 h at the same temperature, after which the solution was cooled and filtered. When the bright yellow

[†]s = singlet, d = doublet, t = triplet, dt = doublet of a triplet. The same representation is used for the other complexes.

filtrate was concentrated under *vacuo*, the desired compound precipitated as pale yellow solid. The compound was filtered, washed with chloroform (20 mL), cold methanol (1 × 5 mL), and diethylether (2 × 15 mL), dried and stored in a desiccator.

The identity and the purity of the final complexes were confirmed by using ^{1}H NMR, ^{13}C NMR, ^{195}Pt NMR, elemental analyses, Infrared (IR), and mass spectroscopy. The ^{1}H NMR spectra obtained show similarity in the aromatic region. Presence of a peak at −2700 ppm on the ^{195}Pt NMR spectra confirms the Pt(NNN) coordination.

(Pttpyeg): Yield: 35 mg (55%), pale yellow powder. ^{1}H NMR (400 MHz, CD_3OH) δ/ppm: 10.23 (2H, d, 6 6″), 9.79 (2H, d, 3 3″), 9.78 (t, 2H, 4 4″), 9.39 (2H, s, 3′ 5′), 9.20 (t, 2H, 5 5″), 5.88 (t, 2H, CH2), 5.44 (t, 2H, CH2). ^{195}Pt NMR (CD_3OH) δ/ppm: −2715. IR (4000–650 cm^{-1}) υ: 3237 (O–H), 3062 (C–H stretch), 1607 (C=H, pyridine), 1476–1423 (C–H stretch), 1222.43 (C–O), 788 (C–H stretch). Anal. Calcd for $C_{17}H_{15}Cl_2N_3O_2Pt$: C, 36.51; H, 2.70; N, 7.51; Found: C, 36.38; H, 3.10; N, 7.92. TOF MS-ES+, *m/z*: 524.0482 $(M + 1)^+$.

(Pttpydeg): Yield: 46 mg (64%), crystalline yellow powder. ^{1}H NMR (400 MHz, CD_3OH) δ/ppm: 9.76 (d, 2H, 6 6″), 9.67 (d, 4H, 3 3″), 9.65 (t, 2H, 4 4″), 9.17 (s, 2H, 3′ 5′), 9.07 (t, 2H, 5 5″), 5.87 (t, 2H, CH2), 5.38 (t, 2H, CH2), 5.21 (t, 2H, CH2), 5.11 (t, 2H, CH2). ^{13}C NMR (77 MHz, CD_3OH), δ/ppm: 62.26, 69.93, 72.01, 74.07, 112.07, 126.95, 130.28, 142.73, 152.27, 156.70, 159.58, 170.89. ^{195}Pt NMR (CD_3OH) δ/ppm: −2705. IR (4000–650 cm^{-1}) υ: 3338 (O–H), 3071 (C–H stretch), 1607 (C=H, pyridine), 1476–1430 (C–H stretch), 1219 (C–O), 773 (C–H stretch). Anal. Calcd for $C_{19}H_{21}Cl_2N_3O_4Pt$: C, 36.73; H, 3.41; N, 6.76; Found: C, 36.35; H, 3.75; N, 6.34. TOF MS-ES+, *m/z*: 568.0847 $(M + 1)^+$.

(Pttpyteg): Yield: 38 mg, dark orange powder (60%). ^{1}H NMR (400 MHz, CD_3OH) δ/ppm: 9.98 (dd, 2H, 6 6″), 9.73 (s, 2H, 3′ 5′), 9.71 (d, 2H, 3 3″), 9.29 (t, 2H, 4 4″), 9.13 (t, 2H, 5 5″), 5.90 (t, 2H, CH2), 5.40 (t, 2H, CH2), 5.22 (m, 2H, CH2), 5.14 (t, 2H, CH2), 5.11 (t, 2H, CH2), 5.04 (t, 2H, CH2). ^{195}Pt NMR (CD_3OH) δ/ppm: −2708. IR (4000–650 cm^{-1}) υ: 3332 (O–H), 3071 (C–H stretch), 1607 (C=H, pyridine), 1448–1429 (C–H stretch), 1220 (C–O), 774 (C–H stretch). Anal. Calcd for $C_{21}H_{23}Cl_2N_3O_4Pt$: C, 38.96; H, 3.58; N, 6.49; Found: C, 38.48; H, 3.41; N, 6.32. TOF MS-ES+, *m/z*: 612.1027 $(M + 1)^+$.

(Pttpytteg): Yield: 30 mg (65%), mustard yellow powder. ^{1}H NMR (400 MHz, CD_3OH) δ/ppm: 8.75 (d, 2H, 6 6″), 8.60 (d, 2H, 3 3″), 8.49 (t, 2H, 4 4″), 8.25 (s, 2H, 3′ 5′), 7.90 (t, 2H, 5 5″), 4.51 (t, 2H, CH2), 3.90 (t, 2H, CH2), 3.67 (t, 2H, CH2), 3.60 (t, 2H, CH2), 3.53 (m, 4H, CH2), 3.47 (t, 2H, CH2), 3.40 (t, 2H, CH2). ^{13}C NMR (77 MHz, CD_3OH), δ/ppm: 39.4, 40.7, 41.0, 60.7, 70.2, 70.4, 70.5, 72.8, 111.2, 125.3, 126.3, 129.9, 143.2, 155.9 158.9, 169.5. ^{195}Pt NMR (CD_3OH) δ/ppm: −2710. IR (4000–650 cm^{-1}) υ: 3246 (O–H), 3064 (C–H stretch), 1607 (C=H, pyridine), 1476–1423 (C–H stretch), 1220 (C–O), 773 (C–H stretch). Anal. Calcd for $C_{23}H_{27}Cl_2N_3O_5Pt$: C, 39.95; H, 3.94; N, 6.08; Found: C, 40.27; H, 3.57; N, 5.60. TOF MS-ES+, *m/z*: 657.1368 $(M + 1)^+$.

Physical measurements

^{1}H NMR and ^{13}C NMR were recorded on either a Bruker Avance DPX 400 or 500 MHz spectrometer at 303 K, using $Si(CH_3)_4$ as the reference for the chemical shifts. ^{195}Pt NMR was done on a 500 MHz spectrometer (^{195}Pt, 107.5 MHz) with chemical shifts externally referenced to $K_2[PtCl_6]$. Low-resolution electron spray ionization mass spectra were recorded on a TOF Micromass spectrometer. IR spectra were recorded by using a Perkin Elmer Spectrum 100 FTIR spectrometer. Elemental analyses were performed by a Thermal

Scientific Flash 2000. Kinetic analyses were studied on an Applied Photophysics SX 20 stopped-flow reaction analyzer coupled with an online data acquisition system with controlled temperature within ±0.1 °C. The wavelengths for the kinetic analysis were predetermined on a Varian Cary 100 Bio UV/visible spectrophotometer with an attached Varian Peltier temperature controller and an online kinetic application. X-ray crystal structure for the ligand qpy was solved using an Oxford Diffraction Xcalibur 2 CCD 4-circle diffractometer linked to an Oxford Cryostat System. The data collection was done at 100 K.

Computational modeling

Computational modeling for the complexes was performed at density functional theoretical (DFT) level based on B3LYP/LanL2DZ [51–53] (Los Alamos National Laboratory 2 double ξ) level theory, with inner core electrons of Pt replaced by relative effective core potential. Due to low electronic spin of Pt(II), the DFT calculations of the complexes were done at singlet state. The complexes were computed in methanol solution taking into account the solvolysis effect by means of the Conductor Polarizable Continum Model [54, 55]. The Gaussian09 suite of programs was used for all computational calculations [56].

Kinetic analyses

All kinetic measurements were performed under *pseudo*-first-order conditions using at least 10-fold excess of the nucleophile in 0.02 M ionic solution, made by dissolving the required amount of $LiCF_3SO_3$ (0.018 M) and LiCl (0.002 M) in dry methanol. LiCl was added to suppress the solvolysis reactions. Since $CF_3SO_3^-$ does not coordinate with Pt(II) [57], all substitution kinetics were studied in this media.

Pt(II) complex solutions were prepared by dissolving the required amount of the complex in the ionic solution. Nucleophile solutions were prepared at 50 times the concentration of the Pt(II) complex. Subsequent dilutions of the nucleophile stock solution afforded solutions of 10, 20, 30, and 40 times the concentration of metal complex. The wavelengths chosen for the kinetic investigations were predetermined using UV/visible absorption spectra (see table S1, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.957200). A typical kinetic trace for the reaction of **Pttpydeg** with TU at 330 nm and 298 K is shown in figure S1.

Substitution reactions were fast, and were studied on an Applied Photophysics SX 20 stopped-flow system coupled with an online data acquisition system. All measurements were carried out in a thermostatted environment to within ±0.1 °C. All data were graphically analyzed using the software package, Origin 7.5® [58], to determine the observed rate constants, k_{obs}. All kinetic data obtained were fitted to first-order exponential decay functions to generate the observed *pseudo*-first-order rate constants, (k_{obs}), using equation (1) [59] at all concentrations and temperatures.

$$A_t = A_0 + (A_0 - A_\alpha)\exp(-k_{obs}t) \quad (1)$$

where A_0, A_t, and A_∞ represent the absorbance of the reaction mixture initially, at time, t and at the end of the reaction, respectively.

The observed rate constants, k_{obs}, for the nucleophiles at different concentrations were determined in the same manner. The values used were averages of 7–10 independent runs. Linear graphs with zero intercepts were obtained for the nucleophiles studied. The second-order rate constants, k_2, for the reactions of the platinum complexes with the nucleophiles

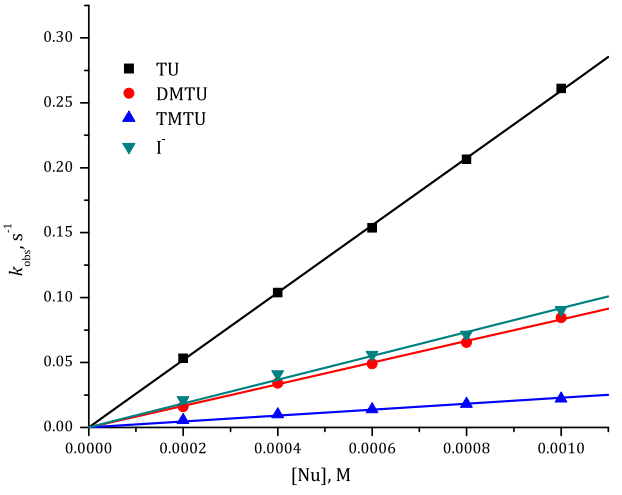


Figure 2. Dependence of the *pseudo*-first-order rate constants (k_{obs}) on the concentrations of the nucleophiles for the chloride substitution from **Pttpydeg** (4.0×10^{-5} M) in methanol solution ($I = 0.02$ M) at 298 K.

were obtained from the slopes and the intercepts of the graphs of k_{obs} *versus* the concentration of the nucleophiles (equation (2) [59]. Representative plots for **Pttpydeg**, shown in figure 2, clearly indicate that the substitution reactions were first order with respect to the incoming nucleophile.

$$k_{obs} = k_2[\mathrm{Nu}] \tag{2}$$

where k_2 is the second-order rate constant.

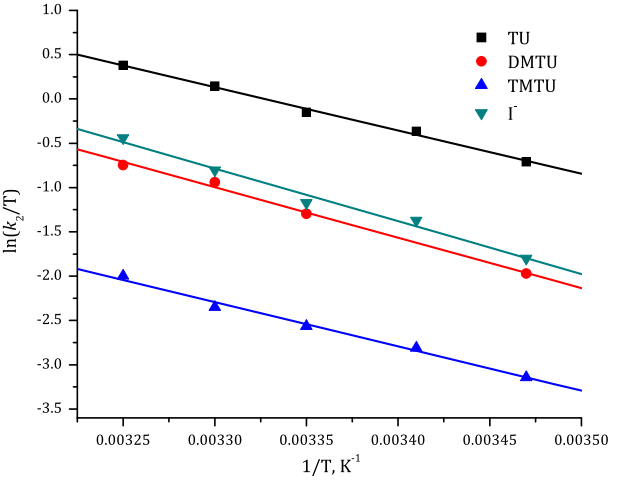


Figure 3. Eyring plots obtained for **Pttpydeg** with the nucleophiles for the forward reactions over the temperature range 15–35 °C.

The temperature dependence studies were done in a similar manner using a single nucleophile concentration in the temperature range of 15–40 °C in 5 °C intervals. The activation parameters, entropy of activation ($\Delta S^{\#}$), and enthalpy of activation ($\Delta H^{\#}$) were obtained using the Eyring equation [59]. Figure 3 shows representative plots obtained for **Pttpydeg** with the nucleophiles for the forward reactions with the nucleophiles.

Results and discussion

Synthesis and characterization

In this study, four square-planar 4′-functionalized Pt(II) terpyridine complexes of polyethylene glycoxy pendant groups, which vary by the number of appended ethylene glycoxy units or monomers, were synthesized and characterized. The ligands have been synthesized by different methods [48, 49, 60]. Details of the synthesis and the spectroscopic data were given in the experimental section. The spectroscopic data obtained were in good agreement with the literature [52, 61] and the proposed chemical structures of the ligands and the complexes. To avoid formation of the diterpyridine ligand, ethylene glycol reagent was added in large excess [49]. Representative ^{1}H NMR, ^{13}C NMR, ^{195}Pt NMR, IR, and mass spectra are given in figures S10–S34 (Supporting Information). The peak due to the OH proton is not seen in any of the ^{1}H NMR spectra due to the proton exchange with the solvent, methanol [62]. The ^{195}Pt NMR signals for all the complexes appeared at −2700 ppm, typical for N^N^N coordinated square-planar Pt(II) center [45, 61]. Furthermore, the IR spectra of the complexes show distinct broad bands at 3200–3300 cm^{-1}, due to the O–H stretches along with the C–H peaks at 3000 cm^{-1} [63, 64]. Additionally, the crystal structure obtained for **Pttpydeg** (figure S35) confirms the synthesis of the anticipated complex. However, the compound could not be resolved to a satisfactory quality due to desolvation.

DFT calculations

In order to obtain further insight on how the ethylene glycoxy pendant groups influence the substitution kinetics of the Pt(II) complexes, the electronic properties of the complexes were investigated at the DFT level. The DFT-calculated geometry optimized structures along with the DFT-calculated data are given in figure 4 and table 1, respectively. Table S3 (Supporting Information) shows that the geometry at the Pt(II) center is slightly distorted square planar which is common to **Pttpy** type complexes [10, 13].

When comparing the DFT calculated natural bond orbital (NBO) charges on the platinum to N_{trans} of **Pttpy** and **Pttpyeg**, the value for platinum decreases from **Pttpy** to **Pttpyeg**. The same is true for the charge on N_{trans}, i.e. it becomes more negative. This difference can be linked to the attachment of ethylene glycoxy pendant to the 4′-position of the parent **Pttpy** molecule. However, when the NBO charges of the corresponding atoms of the ethylene glycoxy appended molecules (i.e. **Pttpyeg** to **Pttpytteg**) are compared, the values are observed to be constant. The results show that the inductive effect to the 4′-position of the complex is limited to the first glycoxy unit only. The subsequent units have little or no effect. This implies that the electronic effect beyond the first unit has little or no influence on the reactivity of the complexes.

Since reactivity parameters are explained by various associated electronic structure principles, the DFT calculated computational data was further analyzed to understand the global

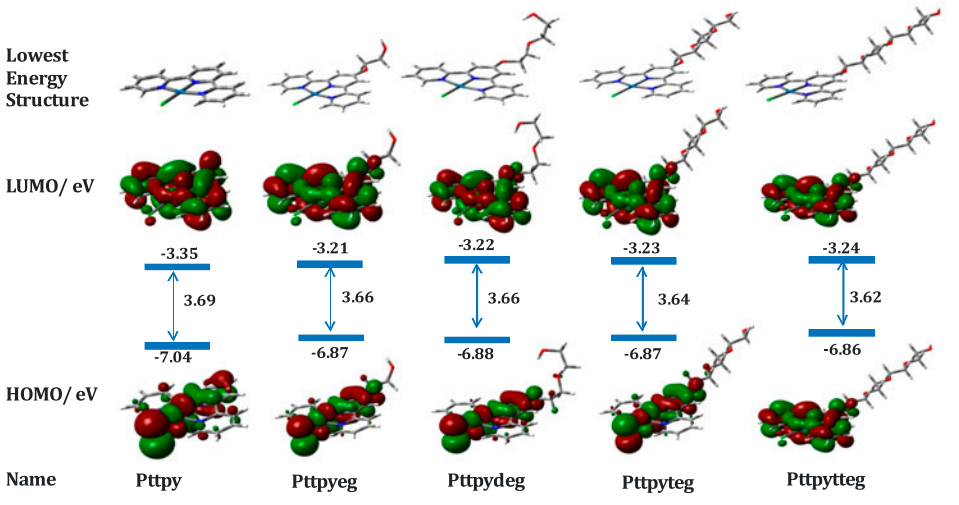


Figure 4. DFT-calculated minimum energy structures, frontier molecular orbitals (HOMO and LUMO), and the planarity of the complexes investigated. Included is the data obtained for the DFT calculated **Pttpy** complex for comparison.

Table 1. Summary of DFT calculated data for the complexes investigated. Included is the data obtained for the DFT calculated **Pttpy** complex for comparisons.

Complex	**Pttpy**	**Pttpyeg**	**Pttpydeg**	**Pttpyteg**	**Pttpytteg**
Bond lengths (Å)					
Pt1–Cl	2.446	2.445	2.446	2.446	2.446
Pt–N1(trans)	1.961	1.961	1.961	1.961	1.961
4′C–O1		1.368	1.368	1.368	1.386
N_{trans}–O1		4.111	4.110	4.110	4.121
Bond angles (°)					
Elevation angle of ethylene glycoxy pendant (α)		37.55	36.44	19.38	17.32
NBO charges					
Pt1	0.604	0.592	0.591	0.591	0.590
N1(*trans*)	−0.453	−0.471	−0.470	−0.471	−0.470
Cl	−0.502	−0.505	−0.505	−0.505	−0.504
$E_{HOMO/eV}$	−7.04	−6.87	−6.88	−6.87	−6.86
$E_{LUMO/eV}$	−3.35	−3.21	−3.22	−3.23	−3.24
ΔE	3.69	3.66	3.66	3.64	3.62
Dipole moment	13.30	11.21	10.72	6.83	4.20
η/eV	1.85	1.83	1.83	1.82	1.81
μ/eV	−5.20	5.04	−5.05	−5.05	5.05
ω/eV	7.31	6.94	6.97	7.00	7.05

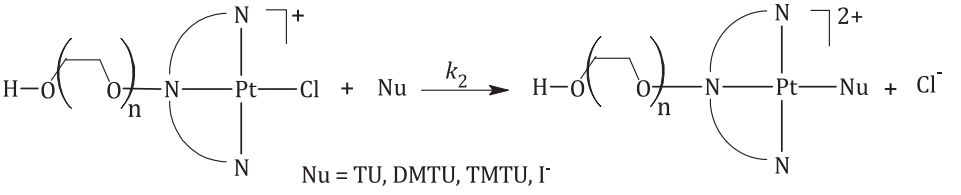
chemical reactivity descriptors [65], such as chemical hardness (η, which relates to the thermodynamic stability of the molecule) [66], electronic chemical potential (μ, which defines the electronegativity of the molecule), and electrophilicity index (ω, which measures the propensity of a species to accept electrons) [67–69]. DFT-calculated μ and ω further support the observed changes in the NBO charges as already discussed. The electrophilicity index shows that the ability of the complex to accept electron decreases from **Pttpy** to **Pttpyeg**,

after which it remains constant. This is an indication of reduction of π-backbonding ability of the terpyridine moiety from **Pttpy** to **Pttpyeg** due to the introduction of ethylene glycoxy pendant.

Kinetics

Substitution kinetics of coordinated chloride from the Pt(II) complexes by four different nucleophiles, i.e. TU, DMTU, TMTU, and an ionic nucleophile, I^- were studied under *pseudo*-first-order conditions using the conventional stopped-flow technique. Only one step, taken to be the substitution of the chloride, was observed with no solvation pathway. Thus, the proposed substitution mechanism for the complexes studied can be represented as shown in scheme 1. The kinetic data obtained are summarized in table 2.

To understand the role of the polyethylene glycoxy pendant units on the rate of chloride substitutions, the reactivities of **Pttpy** and **Pttpyeg** were compared. The difference between them is the appended ethylene glycoxy pendant group in **Pttpyeg**. When a single ethylene glycoxy pendant group is attached to the 4′-position of the terpyridine chelate ligand, the reactivity of the resultant metal complexes is reduced by almost five times to that of **Pttpy**, showing that the polyethylene glycoxy pendant is acting as a σ-donor including the *trans* phenyl ring as supported by the DFT calculations. Furthermore, through π-resonance effect, the lone pair of electrons on the O1 of the glycoxy pendant is donated towards the Pt(II) center. As can be seen from table 1, the inductive σ-electron donation along with the π-electron contribution from the ethylene glycoxy pendant increases the negative charge on the N_{trans} of **Pttpyeg** compared to **Pttpy**. Consequently, the positive charge on the Pt(II) center decreases marginally from 0.604 **(Pttpy)** to 0.592 **(Pttpyeg)**, indicating that the electron density flow is towards the metal center, and can be attributed to the well-known *trans* effect [70]. As reported previously, electron-donating groups on the ancillary position of terpyridine reduce the positive charge at the metal center, thereby lowering the electrophilicity of the metal center [29, 30, 42, 71, 72]. This observation in this study is supported by the DFT-calculated global electrophilicity index, ω, which clearly indicates that the ability of the parent **Pttpy** to accept the electron density from the incoming nucleophile gets considerably decreased when the ethylene glycoxy pendant unit is attached to the 4′-position of the terpyridine backbone [65, 73, 74]. In addition, from the perspective that a high dipole moment favors higher π-back donation character [75], the observed smaller dipole moment of **Pttpyeg** further supports its lower reactivity relative to **Pttpy**. Additional support is obtained by the energy levels of the HOMO and LUMO. The fact that the LUMO energy of the **Pttpyeg** is slightly raised (−3.21 eV) relative to **Pttpy** (−3.35 eV), makes it difficult



n = 1 in **Pttpyeg**, 2 in **Pttpydeg**, 3 in **Pttpyteg** and 4 in **Pttpytteg**

Scheme 1. Proposed mechanism for the substitution of chloride ligand from the Pt(II) complexes.

Table 2. Summary of second-order rate constants k_2 and activation parameters, with the corresponding standard deviations for the substitution of the chloro ligand by a series of TU nucleophiles and iodide at $I = 0.02$ M $LiCF_3SO_3$, adjusted with LiCl. Given in brackets for TU is the data for **Pttpy** taken from literature [29] and included for comparison.

Complex	Nu	k_2/M^{-1} s^{-1}	$\Delta S^{\#}$/J K^{-1} M^{-1}	$\Delta H^{\#}$/kJ M^{-1}
Pttpy	TU	(1494 ± 10)	(−88 ± 5)	(29 ± 2)
		1421 ± 25	−76 ± 4	35 ± 1
	DMTU	448 ± 10	−73 ± 4	36 ± 1
	TMTU	82 ± 4	−91 ± 8	35 ± 2
	I^-	243 ± 4	−42 ± 11	47 ± 4
Pttpyeg	TU	257 ± 5	−56 ± 6	43 ± 2
	DMTU	81 ± 1	−98 ± 6	33 ± 2
	TMTU	22 ± 1	−57 ± 7	40 ± 2
	I^-	95 ± 2	−32 ± 9	53 ± 3
Pttpydeg	TU	265 ± 1	−66 ± 5	40 ± 2
	DMTU	83 ± 1	−54 ± 9	46 ± 3
	TMTU	23 ± 1	−83 ± 7	41 ± 2
	I^-	91 ± 2	−44 ± 9	48 ± 3
Pttpyteg	TU	277 ± 1	−60 ± 3	41 ± 1
	DMTU	93 ± 1	−57 ± 3	45 ± 1
	TMTU	19 ± 0.3	−65 ± 6	46 ± 2
	I^-	91 ± 1	−48 ± 6	48 ± 2
Pttpytteg	TU	321 ± 4	−67 ± 5	39 ± 2
	DMTU	102 ± 1	−46 ± 2	48 ± 2
	TMTU	13 ± 1	−88 ± 6	40 ± 2
	I^-	156 ± 2	−44 ± 5	48 ± 2

to π-back donate. Thus, reduces the transfer of electron density from the 18-electron five-coordinate Pt(II) d_{xz} orbital into the tridentate terpyridine ligand, thereby making the transition state less stable. This can be reflected on from the observed slightly higher activation enthalpy, $\Delta H^{\#}$ of **Pttpyeg**, which indicates the slightly higher energy barrier associated with the formation of transition state complex. The net effect is the observed decrease in the electron acceptability of the terpyridine moiety in comparison to that of **Pttpy**, resulting in a decreased rate of substitution of chloride in **Pttpyeg**.

This retardation effect observed between **Pttpy** and **Pttpyeg** has also been noted previously by Schmülling *et al.* [76], where an electron-donating methoxy (OCH_3) group was attached to the ancillary ligand of a Pt(II) complex of the form $[Pt\{C_6H_3X(CH_2NMe_2)\}(NC_5H_4SO_3)(H_2O)]$, where X = OMe. The decrease in the reactivity was accounted for in terms of the σ-inductive donation from the methoxy group to the metal center making it less electrophilic. A similar effect due to electron-donating groups attached at the 4′-position of the terpyridine ligand has also been reported previously by Jaganyi *et al.* [29, 42].

Furthermore, the decrease in the rate of substitution of **Pttpyeg** is also attributed to the steric contribution imposed on one side of the Pt(II) coordination sphere by the inclined appended ethylene glycoxy unit (figure 5), thereby hindering the approach of the axially incoming nucleophile. This steric influence exists in **Pttpyeg** since the angle of inclination, α, is absent in **Pttpy**. Therefore, it can be concluded that the difference in the rate of substitution between **Pttpy** and **Pttpyeg** is due to both steric and electronic effects.

The analysis of the reactivity of the other complexes having ethylene glycoxy pendant shows a slight increase in the rate of substitution with the increase in the number of ethylene glycoxy units. One would have expected the reactivity to decrease due to the increase in the σ-inductive effect, however, that is not the case and is supported by the DFT

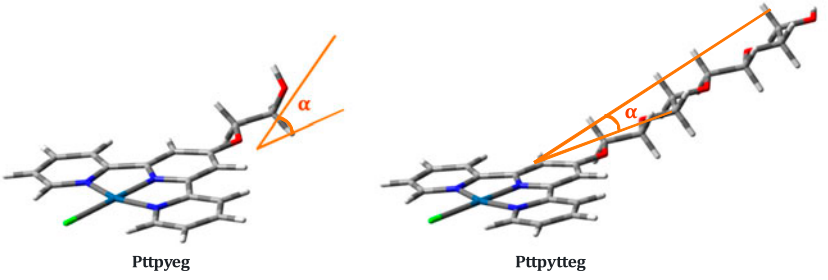


Figure 5. Aerial view showing the angles of inclination, **α**, of the pendant units in the DFT calculated structures of **Pttpyeg** and **Pttpytteg**.

calculations. The observed NBO charges on the Pt(II) center and N_{trans} of **Pttpyeg** to **Pttpytteg** are all constant indicating that no change is being experienced by the Pt(II) centers as the pendant unit is increased. The σ-donation and the π-resonance contribution (due to O1) is effective only up to the first glycol unit. The global electrophilicity index shows a very small increase with an increase in the pendant unit, which might be linked to the increase in electrons within each pendant unit. Therefore, the remaining factor that accounts for the observed reactivity from **Pttpyeg** to **Pttpytteg** is steric hindrance due to inclination of the ethylene glycoxy pendant group to the plane containing Pt(II). This angle α, which has also been reported in the literature by Jaganyi *et al.* [77], when investigating the reactivity of Pt(II) complexes having appended poly alkyl groups, decreases from **Pttpyeg** (37.55°) to **Pttpytteg** (17.32°) as depicted in figure 5. This means that one side of these complexes experiences steric hindrance which decreases as the angle of inclination decreases with increase in the number of pendant units. This results in reactivity increasing slightly from **Pttpyeg** to **Pttpytteg**.

There is also a possibility that very weak intramolecular hydrogen bonding between the lone pair of electrons on the oxygen atoms and the neighboring H atoms or the OH [78–80] might be contributing to the stabilization of the five-coordinate transition state, which increases with the increase in the number of oxygens in the pendant (scheme S1, Supporting Information).

If all the facts are put together, it explains the observed substitution reactivity trend: **Pttpy** >> **Pttpytteg** > **Pttpyteg** > **Pttpydeg** > **Pttpyeg**. If the reactivity of **Pttpy** with TU is taken as a reference, the ratio of reactivity follows: 1.00 : 0.17 : 0.18 : 0.19 : 0.22, respectively, for **Pttpy**, **Pttpyeg**, **Pttpydeg**, **Pttpyteg**, and **Pttpytteg**. The slight changes in reactivity for the ethylene glycoxy pendant complexes are sterically controlled with minor or no electronic effects. If the relative rates for the reactions with TU, DMTU, TMTU, and I^- are compared for the five complexes (for TU : DMTU : TMTU : I^- ion where TMTU is taken as the standard, **Pttpy** 17 : 5.5 : 1 : 3.0; **Pttpyeg** 11.7 : 3.7 : 1 : 4.3; **Ptpydeg** 11.5 : 3.6 : 1 : 3.0; **Pttpyteg** 14.5 : 4.9 : 1 : 4.8; **Pttpytteg** 24.7 : 7.8 : 1 : 12.0), it can clearly be seen that the reactions with **Pttrytteg** are more sensitive to the steric hindrance of the incoming ligands. This is due to the steric hindrance of the inclined ethylene glycoxy pendant in **Pttpytteg** being greater than the other complexes. The sensitivity to the steric hindrance of the incoming nucleophiles decreased as the inclination from the appended pendant decreases.

The data in table 2 clearly show a dependence of the chloride substitution on the steric hindrance of the incoming nucleophiles. In all cases, TU has the highest rate constant and the rate constant decreases as the incoming nucleophile gets more bulky; i.e. rate constants

for DMTU and TMTU are significantly lower compared to TU. The results show that the complexes are sensitive to the steric hindrance of the incoming nucleophiles which is typical of an associative substitution reaction. To compare the reactivity of the neutral nucleophiles with an anionic nucleophile, I^- was used. In case of the ionic nucleophile, I^-, the rate of substitution of the chloride was slower than TU. This difference in reactivity has been explained to be a result of the electrostatic attraction between the anionic iodide and the cationic metal center facilitated by the high polarisability of I^- [77].

The activation parameters obtained for the substitution of the chloride support an associative mode of mechanism [29]. The large and negative entropy of activation ($\Delta S^{\#}$) suggests a more ordered transition state. The small enthalpies of activation ($\Delta H^{\#}$) support the ease of bond formation in the transition state [21, 29]. This is typical for substitution of d^8 square planar Pt(II) complexes [21, 42, 45, 77, 79, 81].

Conclusion

This study demonstrates that the polyethylene glyoxy pendant attached *trans* to the leaving group of **Pttpy** which acts as an σ-donor towards the Pt(II) center, thereby decreasing the reactivity compared to the parent **Pttpy**. The σ-donation due to the pendant unit and π-electronic contribution due to O1 are effective only up to one unit of the ethylene glycoxy pendant, beyond which there is no significant electronic effect on the Pt(II) metal center. Thus, the retardation of the reactivity from **Pttpy** to **Pttpyeg** is mostly due to both steric and electronic effects caused by the appended ethylene glycoxy pendant. However, the slight increase in substitution reactivity from **Pttpyeg** to **Pttpytteg** is mainly sterically controlled, as the angle of inclination of the appended ethylene glycoxy pendant decreases from the Pt(II) plane. The complexes are sensitive to the incoming nucleophiles as demonstrated by the decrease in rate constant depending on the size. The activation parameters, enthalpy of activation, and entropy of activation, well support an associative mode of mechanism, where bond formation in the transition state is favored.

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