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Ruthenium(II) Complexes of Tetra-2-pyridyl-1,4-diazine

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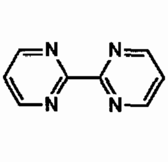
Abstract

Tetra-2-pyridyl-1,4-diazine (TPD) reacts with one equivalent of $Ru(tpy)Cl_3$ to provide $(tpy)Ru(TPD)^{2+}$ which when treated with a second equivalent of $Ru(tpy)Cl_3$ under more forcing conditions provides the TPD bridged binuclear complex, $(tpy)Ru(TPD)Ru(tpy)^{4+}$. The structure of both complexes, particularly with regard to planarity of the pendant pyridine rings is analyzed by high field NMR. The electronic spectrum of the binuclear complex shows pronounced bathochromic shift, while the redox potentials for $(tpy)Ru(TPD)^{2+}$ indicate a diminished HOMO–LUMO energy gap.

Introduction

A recent outgrowth of the very fertile area of ruthenium(II) tris-diamine chemistry has been the study of polynuclear complexes which might mimic the behavior of the parent system, $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) while allowing for the transfer of more than one electron from the photoexcited state. The design of such polynuclear complexes has involved the use of polyaza polyaryl bridging ligands which are generally 'capped' by two or more $Ru(bpy)_2$ subunits [1–8]. The simplest example of such a bridging ligand would be 2,2′-bipyrimidine (**1**) which incorporates two bipyridine-like chelating sites in the same biaryl ligand so that each aromatic ring is bridging [6, 7]. Other related systems are 2,3-di-2-pyridylpyrazine (**2**) [1, 2] and its benzo-fused analog 2,3-bis(2-pyridyl)quinoxaline (**3**) [3–5]. These ligands bridge the metal centers through only one ligating site, the diazine ring.

Although 2,2′;6′,2″-terpyridine (tpy) forms a wide variety of bis-complexes with ruthenium(II) and other d_6 metals, its coordination chemistry has been less widely studied. This lack of study is due to its relatively short-lived excited state at 298 K which presumably limits photocatalytic activity. Quite recently Potts and coworkers have shown that polymer supported terpyridines may overcome some of these difficulties [9].



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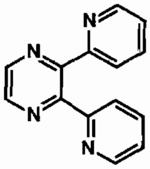

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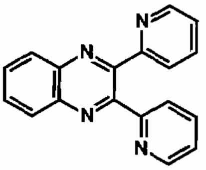

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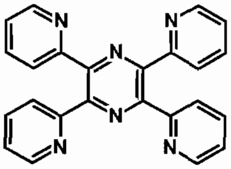
We have become interested in the properties of ruthenium terpyridyl complexes [10, 11] and in this paper we report the use of tetra-2-pyridyl-1,4-diazine (TPD, **4**) as a bridging ligand. TPD is analogous to 2,2′-bipyrimidine in that it is the simplest neutral ligand which incorporates two tridentate sites in a symmetrical arrangement. Bridging would be accomplished through the central 1,4-diazine ring which could bind two metals simultaneously. In 1959 Goodwin and Lions first reported on the use of TPD as a tridentate ligand but they claimed that it could not function as a bis-tridentate [12].



4 (TPD)

They attributed this inability to form binuclear complexes to the supposed reluctance of the four pendant 2-pyridyl rings to become coplanar with the central diazine ring, a condition which they presumed to be essential for effective complexation. We have examined the ruthenium(II) complexes of a series of 3,3′;5′,3″-bis-annelated terpyridines to determine the conformational requirements for effective tris-coordination. Analysis of the X-ray structure of a bis-tetramethylene bridged derivative demonstrates that complexation can occur even when the dihedral angle between two adjacent pyridine rings is greater than 35° [10]. This knowledge, along with the apparent ability of **2** and **3** to form binuclear complexes which would exhibit the same sort of steric crowding as TPD, inspired us to re-examine **4** as a potential bridging ligand.

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Synthesis

Goodwin and Lions demonstrated that TPD would form mononuclear bis-complexes with Ru(II), Fe(II), Co(II) and Ni(II) but did not observe polymer formation even under forcing conditions (glycerol, 180°) [12]. We repeated the experiment using $RuCl_3 \cdot 3H_2O$ in 1:1 refluxing ethanol/H_2O and obtained the same complex, $Ru(TPD)_2^{2+}$, as its PF_6 salt. In order to encourage the formation of a binuclear complex, we first treated TPD with excess $Ru(tpy)Cl_3$ in 1:1 refluxing ethanol/H_2O to afford $(tpy)Ru(TPD)[PF_6]_2$. Reaction of this complex with additional $Ru(tpy)Cl_3$ in refluxing 1:1 1-propanol/H_2O afforded a 32% yield of the complex $(tpy)Ru(TPD)Ru(tpy)[PF_6]_4$. When the reaction between TPD and $Ru(tpy)Cl_3$ is carried out directly in refluxing 1:1 1-propanol/H_2O, the same complex is obtained but in low yield as part of a mixture of products.

$$\mathrm{TPD} \xrightarrow{\mathrm{Ru(tpy)Cl_3}} \mathrm{(tpy)Ru(TPD)^{2+}} \xrightarrow{\mathrm{Ru(tpy)Cl_3}} \mathrm{(tpy)Ru(TPD)Ru(tpy)^{4+}}$$

Spectral and Electrochemical Properties

The TPD complexes were characterized primarily on the basis of their NMR spectra and elemental analyses. In earlier work on ruthenium bipyridyl and terpyridyl complexes we have found that ^1H NMR chemical shift data can be diagnostic of both structure and conformation [10, 13]. Because of high symmetry, the binuclear complex $(tpy)Ru(TPD)Ru(tpy)^{4+}$ shows only 10 signals in its NMR spectrum. As may be seen in Fig. 1, these signals are reasonably well resolved and could be readily assigned by comparison with related spectra as summarized in Table I. A further simplifying feature of these spectra is the fact that the complexes contain two or three independent spin systems so that well resolved, essentially first order behavior is observed [14]. The enhancement of peak intensities in the direction of nuclei which are coupled to one another further facilitates assignments.

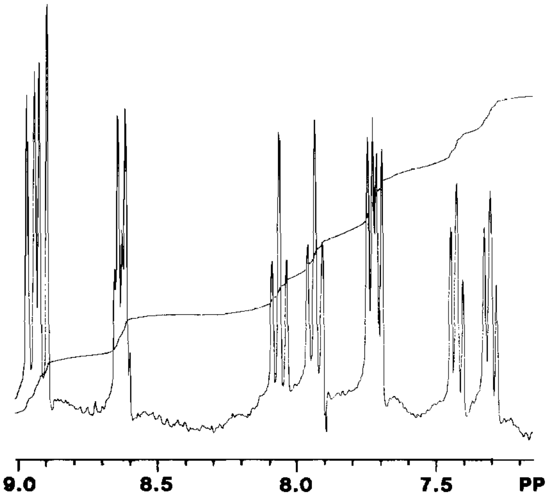

Fig. 1. 300 MHz ^1H NMR spectrum of $(tpy)Ru(TPD)Ru(tpy)[PF_6]_4$ in CD_3CN at 30 °C.

Several features of these NMR spectra are noteworthy. In comparing the free ligands, the resonance for H_3 is shifted upfield by 0.57 ppm for TPD as compared to tpy. This difference results from shielding of H_3 by the adjacent pyridine ring. The H_4 proton feels this same effect but to a lesser extent. When TPD is complexed with ruthenium, $H_{3'}$ resonates at 7.64 ppm, considerably higher than the 8.50 ppm observed in the corresponding tpy complex. Presumably the complexed pyridine ring is held in the plane of the diazine ring forcing the adjacent uncomplexed pyridine ring to rotate out of this plane where it has a stronger shielding effect on $H_{3'}$. When both halves of TPD are complexed by ruthenium as in $(tpy)Ru(TPD)Ru(tpy)^{4+}$, the two adjacent pyridine rings of TPD are forced into a more coplanar arrangement and $H_{3'}$ is no longer shielded but rather is *deshielded*, resonating 1.31 ppm

TABLE I. ^1H NMR Data for 2,2′;6′,2″-Terpyridine and Tetra-2-pyridyl-1,4-diazine (TPD) and their Ruthenium(II) Complexes[a]

Compound	Terpyridine						TPD[b]							
	H_3	H_4	H_5	H_6	$H_{3'}$	$H_{4'}$	H_3	H_4	H_5	H_6	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{6'}$
tpy	8.62	7.86	7.33	8.70	8.46	7.96								
$Ru(tpy)_2^{2+}$	8.50	7.92	7.17	7.34	8.76	8.42								
TPD							8.05	7.80	7.23	8.38				
$Ru(TPD)_2^{2+}$							8.39	8.24	7.74	8.73	7.64	7.65	7.22	7.57
$(TPD)[Ru(tpy)]_2^{4+}$	8.63	8.06	7.42	7.73	8.91	8.62					8.95	7.93	7.30	7.70

[a] Chemical shifts in ppm downfield from Me_4Si. Spectra were obtained at 300 MHz in $CDCl_3$ (ligands) and CD_3CN (complexes). No appreciable solvent shift was observed. [b] For TPD, primed numbers correspond to coordinated pyridine and unprimed numbers correspond to uncoordinated pyridine rings.

downfield at δ8.95. It is interesting that in this same complex H_6 of tpy and $H_{6'}$ of TPD have nearly identical chemical shifts, reflecting the fact that they occupy very similar environments.

The electronic absorption spectra for the three ruthenium TPD complexes are illustrated in Fig. 2. The absorption maximum for $Ru(tpy)_2^{2+}$ occurs at 475 nm ($\epsilon = 16{,}200$) and is omitted from Fig. 2 for clarity. Several interesting features are in evidence. First, the absorption energy of $Ru(TPD)_2^{2+}$ is identical to that of $Ru(tpy)_2^{2+}$ although somewhat more intense. It has been clearly established for ruthenium tris-diimine complexes that the UV absorption energy decreases as the delocalizing ability of the ligands increases. Mixed diimine complexes of the type RuA_2B^{2+} generally show distinct components for metal to ligand charge transfer (MLCT) into ligands A and B [15]. These same effects have not yet been established for ruthenium terpyridine complexes. McMillan and coworkers have examined symmetrical ruthenium complexes of several phenyl substituted terpyridines but no general trend was obvious [16]. However, they did determine, that a 4′-phenyl substituent red-shifted the absorption maximum by 20 nm. We can surmise that the influence of the four non-coordinated pyridyl rings in $Ru(TPD)_2^{2+}$ is diminished due to their being rotated out of the plane of the diazine ring. The resulting electron withdrawing effect must be offset by an increased donating effect of the diazine ring.

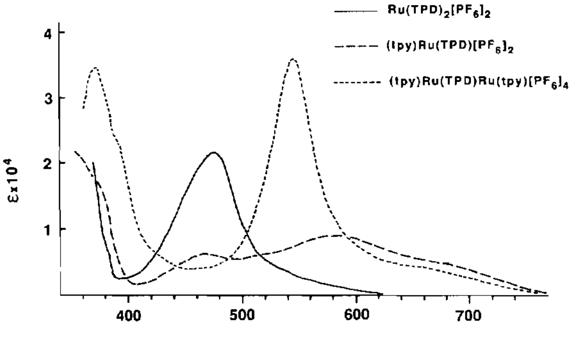

Fig. 2. Electronic absorption spectra of ruthenium TPD complexes, 5×10^{-5} M in CH_3CN.

More surprising is the spectrum of the mixed complex $(tpy)Ru(TPD)^{2+}$. Our intuition from analogous bipyridine chemistry would predict that the absorption maximum should appear at the same energy as the two symmetrical complexes. We do observe a small component at 470 nm as well as a very broad band of relatively low intensity centered at 580 nm. Although d–π* transitions are invoked to explain MLCT absorption for ruthenium diimine complexes, it appears that the same logic may not be valid for these triimine systems. Further studies on a family of unsymmetrical Ru(II) triimine complexes are underway in hopes of elucidating this question.

The binuclear complex, $(tpy)Ru(TPD)Ru(tpy)^{4+}$, behaves more conventionally, showing a single strong absorption at 543 nm, red-shifted about 70 nm from either of the symmetrical mononuclear complexes. Similar shifts have been observed for MLCT into the bridging ligand of dimeric Ru(II) diimine complexes [1].

Table II summarizes the half-wave potentials for the ruthenium complexes under discussion and Fig. 3 illustrates the cyclic voltammograms for the TPD complexes. In considering the oxidation potentials, we find that $Ru(TPD)_2^{2+}$ is 0.27 V more difficult to oxidize than $Ru(tpy)_2^{2+}$. Although the difference between the anodic and cathodic peak potentials is somewhat greater than the theoretical value of 59 mV [17], this process appears to be at least quasi-reversible. Oxidation of the unsymmetrical mononuclear complex, however, occurs at surprisingly low potential where a value intermediate between 1.27 and 1.54 would have been predicted. Unsymmetrical ruthenium tris-diimine complexes do not generally show such a dramatic lowering of their oxidation potentials as compared to their symmetrical analogs [13b]. The implication is that for this system the energy of the Ru(II) t_2 orbital has been significantly raised. The binuclear complex shows two oxidation waves representing formation of the Ru(II)–Ru(III) and Ru(III)–Ru(III) species. The first oxidation is quite consistent

TABLE II. Half-wave Potentials for Ruthenium Complexes[a]

Complex	$E_{1/2}$ (V)	
	oxidation	reduction
$Ru(tpy)_2^{2+}$	+1.27(70)	−1.27(70), −1.51(90)
$Ru(TPD)_2^{2+}$	+1.54(80)	−0.83(70), −1.07(80)
$(tpy)Ru(TPD)^{2+}$	+1.04(90)	−0.48(60), −0.95(100)
$(tpy)Ru(TPD)Ru(tpy)^{4+}$	+1.05(70), +1.43(80)	−0.33(80), −0.80(70), −1.38(120)

[a] Potentials are given in volts *vs.* SCE for saturated CH_3CN solutions, 0.1 M in TBAP recorded at 25 ± 1 °C. The difference between cathodic and anodic peak potentials (mV) is given in parenthesis.

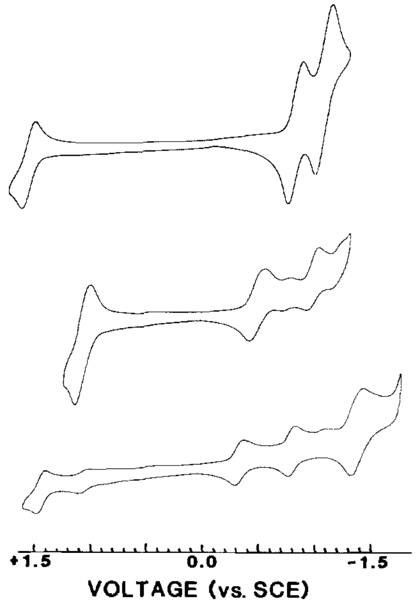

Fig. 3. Cyclic voltammograms of ruthenium TPD complexes as saturated solutions in CH_3CN containing 0.1 M TBAP at 25 °C with a sweep rate of 200 mV/s: $Ru(TPD)_2[PF_6]_2$, top; $(tpy)Ru(TPD)[PF_6]_2$, middle; $(tpy)Ru(TPD)Ru(tpy)[PF_6]_4$, bottom.

with what is observed for $(tpy)Ru(TPD)^{2+}$. Both waves are quasi-reversible.

The reduction of these complexes exhibits an even more dramatic change in potential. It is not surprising that the reduction of $Ru(TPD)_2{}^{2+}$ should occur more readily than $Ru(tpy)_2{}^{2+}$ since lower energy π^* orbitals would be expected for the former species. The first reduction wave for the mixed complex $(tpy)Ru(TPD)^{2+}$ shows a substantial shift to more positive potential which is again inconsistent with ruthenium tris-diimine complexes where much smaller perturbations are observed. The decreased difference between the oxidation and reduction potentials for $(tpy)Ru(TPD)^{2+}$ is readily apparent in Fig. 3 and is consistent with the diminished HOMO–LUMO energy gap implied by the substantially longer wavelength electronic absorption for this species. The first reduction for the binuclear complex is even more positive but this behavior is typical for Ru(II) binuclear tris-diimine complexes [1]. We hope that studies of other unsymmetrical Ru(II) terpyridine type complexes will help to further elucidate the behavior of these systems.

Experimental

Nuclear magnetic resonance spectra were recorded on a Nicolet NT-300 WB spectrometer in CD_3CN or $CDCl_3$ with chemical shifts reported in parts per million downfield from $(CH_3)_4Si$. Electronic absorption spectra were recorded on a Perkin-Elmer 330 spectrophotometer. FAB mass spectra were obtained on a VG 70-SEQ mass spectrometer using *m*-nitrobenzylalcohol as a matrix. The preparation of 2,3,5,6-tetra-(2′-pyridyl)-1,4-diazine (TPD) has been previously reported [12].

Cyclic voltammograms were recorded using a BAS CV-27 voltammograph and a Houston Instruments Model 100 X-Y recorder. A three electrode system was employed consisting of a platinum button working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode. The reference electrode was separated from the bulk of the solution by a cracked glass bridge filled with 0.1 M TBAP in acetonitrile. Deaeration of all solutions was performed by passing high purity nitrogen through the solution for five minutes and maintaining a blanket of nitrogen over the solution while making measurements. Reagent grade acetonitrile was distilled twice from P_2O_5 under nitrogen. The supporting electrolyte, tetra-n-butylammonium perchlorate (TBAP), was recrystallized from EtOAc/hexane, dried, and stored in a dessicator. Half wave potentials were calculated as an average of the cathodic and anodic peak potentials [17].

Ru(TPD)₂[PF₆]₂

A mixture of 582 mg (1.5 mmol) of 2,3,5,6-tetra-(2′-pyridyl)-1,4-diazine (TPD) and 132 mg (0.5 mmol) of $RuCl_3 \cdot 3H_2O$ was refluxed in 60 ml of 1:1 $EtOH/H_2O$ under nitrogen for 48 h. A deep red color developed gradually. The reaction mixture was cooled and an aqueous solution of NH_4PF_6 (2 equiv.) was added. The resulting red precipitate was collected, dried and chromatographed on 60 g of alumina eluting with 1:1 acetonitrile/toluene. Recrystallization from acetonitrile/toluene afforded 320 mg (52%) of $Ru(TPD)_2[PF_6]_2$ as red needles. *Anal.* Calc. for $C_{48}H_{32}F_{12}N_{12}P_2Ru \cdot C_2H_6O$: C, 49.5; H, 3.1; N, 13.9. Found: C, 49.2; H, 2.8; N, 14.4%.

Ru(tpy)(TPD)[PF₆]₂

A mixture of 52 mg (0.134 mmol) of TPD and 118 mg (0.268 mmol) of $Ru(tpy)Cl_3$ [18] in 25 ml of 1:1 $EtOH/H_2O$ was refluxed under nitrogen for 48 h. The reaction mixture was then cooled, filtered, and aqueous NH_4PF_6 (2 equiv.) was added. The resulting blue precipitate was collected, dried and chromatographed on 20 g of alumina eluting with 2:1 acetonitrile/toluene. Recrystallization of the first fraction from acetonitrile/toluene yielded 12 mg of $Ru(tpy)_2[PF_6]_2$ as red needles. The second fraction afforded 110 mg (81%) of $Ru(tpy)(TPD)(PF_6)_2$ as a blue powder which could not be recrystallized. FAB mass spectrum (*m/e*): 868 $[(tpy)Ru(TPD)(PF_6)^+]$, 722 $[(tpy)Ru(TPD)^+]$, 334 $(tpy)Ru^+]$.

(tpy)Ru(TPD)Ru(tpy)[PF_6]$_4$

A mixture of 45 mg (0.045 mmol) of Ru(tpy)(TPD)(PF_6)$_2$ and 40 mg (0.09 mmol) of Ru(tpy)Cl_3 was refluxed under nitrogen in 15 ml of 1:1 n-PrOH/H_2O for 48 h. The reaction mixture was cooled and aqueous NH_4PF_6 (4 equiv.) was added. The dark purple precipitate was collected, dried, and recrystallized from acetonitrile/toluene to afford 24 mg (32%) of (tpy)Ru(TPD)Ru(tpy)[PF_6]$_4$ as purple needles. *Anal.* Calc. for $C_{54}H_{38}F_{24}N_{12}P_4Ru_2 \cdot C_3H_8O$: C, 40.33; H, 2.71; N, 9.91. Found: C, 40.45; H, 2.69; N, 9.89%.

Acknowledgements

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