

Synthesis and Characterization of Rhodium(III) Complexes Bound to the Novel Bridging Ligand 2,3,5,6-Tetra(2-pyridyl)pyrazine (tppz)

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Several nitrogen aromatic heterocyclic ligands, such as 2,3-bis(2-pyridyl)pyrazine (dpp) [1–7], 2,5-bis(2-pyridyl)pyrazine (dppz) and 2,3-bis(2-pyridyl)-1,2,4,5-tetrazine (dptz) [8], 2,3-bis(2-pyridyl)quinoxaline (dpq) [9, 10], 2,2'-bipyrimidine (bpm) [10–16], benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]tripyrazine (HAT) [10, 17, 18], have recently been used to form bidentate mono- and bimetallic complexes with low-spin d^6 metals including Ru(II), Rh(III) and group 6 carbonyls. These complexes possess highly absorbing MLCT transitions in the visible–near UV region of the spectrum, and when the metals in poly-metallic complexes are directly bound through the same ligand ring possessing good π delocalization (such as in pyrazine), metal–metal electronic interaction has been observed [19–21]. Mono- and bimetallic d^6 complexes bound through nitrogen aromatic heterocyclic ligands have thus been prepared and studied as models for photochemically induced excited-state energy-transfer reactions, photochemistry and photophysics of polymetallic complexes and for solvatochromic behavior.

Bimetallic complexes with the novel bis-tridentate ligand 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) have only recently been prepared with Ru(II) centers [22, 23]. We wish to report the preparation and characterization of the first mono- and bimetallic Rh(III) complexes bound with tppz. Synthetically, the Rh(tppz)Cl₃ complex alone is significant as a precursor complex in attempted preparation of bis-poly(pyridyl) complexes of Rh(III) [24].

Experimental

Materials

Analytical reagent grade solvents and compounds were used for preparations and experiments described in this work. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

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Instrumentation

Electronic absorption spectra were recorded on a Varian DMS 300 spectrophotometer with matching quartz cells. Cyclic voltammograms were recorded on a Bio Analytic Systems CV-1B cyclic voltammograph with a Hewlett-Packard 7044A XY recorder. Cyclic voltammograms were recorded in CH₃CN using 0.1 M tetrabutylammonium perchlorate as an electrolyte. The glassy carbon working electrode (3.0-mm diameter) was polished and the solutions were thoroughly deoxygenated prior to each scan. An Ag/AgCl (3 M KCl, nominally –0.044 V versus SCE) reference electrode was used. All potentials are reported versus SCE and are uncorrected for junction potentials. The potentials reported for reduction couples $E_{1/2}$ are estimates obtained by averaging anodic and cathodic peak potentials. Infrared spectra were recorded as solid KBr samples on a Nicolet Model 20DX FTIR from 4000–400 cm⁻¹ using 2 cm⁻¹ resolution. Conductance measurements were recorded using a Yellow Springs Instrument Co. Model 31 conductivity bridge and cells. The cell constant was calibrated using a 0.0200 M KCl aqueous solution at 25 °C with a literature value of 0.002768 ohm⁻¹. Molar conductivities for (RhCl₃)(tppz) and (RhCl₃)₂(tppz) complexes are 10 ± 1 and 36 ± 4 ohm⁻¹ cm² mol⁻¹ respectively, in CH₃CN, and suggest the (RhCl₃)(tppz) and (RhCl₃)₂(tppz) complexes do not ionize in CH₃CN [25]. Aqueous solutions of the complexes exhibit conductivity values indicating substantial aquation occurred.

Synthesis

The tppz ligand was prepared according to the literature method without difficulty [26]. The (RhCl₃)(tppz) and (RhCl₃)₂(tppz) complexes were prepared by mixing 1:2 or 2:1 RhCl₃ to tppz mole ratios in ethanol and methanol respectively, and heating at reflux in an open-top condenser. A precipitate formed in the flask after 1 h, and the solution was maintained at reflux for 24 h. After cooling to room temperature, the mono- or bimetallic solids were collected by filtration, washed with 500 ml of boiling anhydrous methanol or ethanol to remove excess tppz, and vacuum dried. Yield of (RhCl₃)(tppz), 80%. *Anal. Calc.* for C₂₄H₁₆N₆Cl₃Rh: C, 48.22; H, 2.70; N, 14.06. Found: C, 48.19; H, 2.73; N, 14.00%. Yield of (RhCl₃)₂(tppz), 89%. *Anal. Calc.* for C₂₄H₁₆N₆Cl₆Rh₂· $\frac{1}{2}$ CH₃OH: C, 35.75; H, 2.21; N, 10.21. Found: C, 35.83; H, 2.29; N, 10.22%.

Results and Discussion

The (RhCl₃)(tppz) and (RhCl₃)₂(tppz) complexes are only slightly soluble ($M \approx 10^{-4}$) in CH₃CN, H₂O,

CH₃NO and other common solvents. The UV–Vis electronic absorption for (RhCl₃)(tppz) and (RhCl₃)₂(tppz) in acetonitrile are shown in Fig. 1, and the results are summarized in Table 1. The mono- and bimetallic complexes both display intense transitions in the near-UV and blue regions of the spectrum, and are similar to the spectra of Rh(bpy)₃³⁺, Rh(bpy)₂Cl₂⁺ and Rh(bpm)₂Cl₂⁺ [16, 24, 27]. Based on the similarity of (RhCl₃)(tppz) with the free tppz ligand and other Rh(III) complexes, the absorption at 310 nm is assigned as an intraligand $\pi \rightarrow \pi^*$ transition, the 345 nm transition is assigned as an MLCT transition, while the weak shoulder at 400 nm is most likely an LF transition. The (RhCl₃)₂(tppz) spectrum is also dominated by MLCT transitions at 370 and

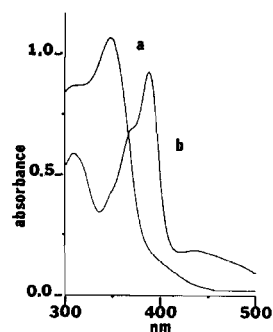


Fig. 1. Electronic absorption spectra of (a) 4.0×10^{-5} M (RhCl₃)tppz and (b) 2.8×10^{-5} M (RhCl₃)₂tppz, in acetonitrile.

390 nm, while the 310 nm absorption is assigned as an intraligand $\pi \rightarrow \pi^*$ transition. The low energy peak at 440 nm is at an energy that might be expected for an LF transition; however, the high extinction coefficient and similarity with lower energy shifts of bi- versus monometallic complexes suggest a low-energy Rh d _{π} \rightarrow tppz p π^* transition.

Cyclic voltammograms for the free tppz free ligand and the monometallic complex were recorded in acetonitrile/0.10 M TBAP. The first reduction of tppz, $E_{1/2}(1)$, was recorded at -1.43 V, and a second reduction wave, $E_{1/2}(2)$, was at -1.73 V versus SCE. Values of $E_{1/2}(1) = -1.38$ V and $E_{1/2}(2) = -1.70$ were recorded for (RhCl₃)(tppz). Although the peak-to-peak separation of the waves was 70–125 mV, which is larger than the theoretical 59 mV, based on the equivalence of peak wave heights and repeatability, they are judged to be at least quasi-reversible [28]. The more positive reduction potential of the monometallic complex versus free tppz ligand is as expected for addition of the RhCl₃ electron-withdrawing group onto the tppz ligand. The reduction potential of the bimetallic complex was unobtainable due to low solubility.

Data for the infrared spectra for tppz, and the mono- and bimetallic complexes were obtained as solids in KBr. Predominant vibrations for the free tppz ligand are associated with $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{C})$ and ring stretching. The reported separation between $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ is close to 20 cm⁻¹ for both free bpy and bpm [16, 29], and thus the observed peaks

TABLE 1. Electronic absorption data for some rhodium(III) polypyridyl complexes and electrochemical data for tppz and (RhCl₃)(tppz)

Complex ion	λ_{max} (nm)	ϵ (M ⁻¹ cm ⁻¹) $\times 10^3$	Assignments	Reduction potential ^a	Reference
tppz	310	21	$\pi \rightarrow \pi^*$	-1.43 V $E_{1/2}(1)$ -1.73 V $E_{1/2}(2)$	this work
(RhCl ₃)(tppz)	405sh 348 310	3.0 26 20	LF MLCT $\pi \rightarrow \pi^*$	-1.38 V $E_{1/2}(1)$ -1.70 V $E_{1/2}(2)$	this work
(RhCl ₃) ₂ (tppz)	440 390 370 310	7 31 22 20	MLCT MLCT MLCT $\pi \rightarrow \pi^*$		
<i>cis</i> -(RhCl ₂ bpm ₂) ⁺	390sh 289	0.12 3.3	LF b		10
(Rh ₂ bpm ₃ Cl ₄) ²⁺	399sh 271	1.6 30	LF $\pi \rightarrow \pi^*$		10
(Rh(bpy) ₃) ³⁺	242 305 318	39 39 43	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$		24, 27
(Rh(bpy) ₂ Cl ₂) ⁺	300 312 380	24 27 0.1	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ LF		27

^a $E_{1/2}$ values calculated at scan rates of 100 mV/s; conditions as described in the Experimental section.

^bIntraligand.

for tppz at 1590 and 1567 cm^{-1} may be due to either different $\nu(\text{C}=\text{N})$ on the different tppz (pz and bpy) rings or $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ with coincidental equivalence of the different rings. An intense peak for tppz at 1394 cm^{-1} is typical for ring stretching of both pz and bpy rings. The monometallic complex exhibits broad peaks at 1631, 1600, 1585 and the direction and magnitude of the ν increase is typical when metal centers are bonded to the ligand. Again, because of three similar rings in the unsymmetric monometallic complex (bound py, pz and unbound py), exact assignments are not obtainable. The ring stretching is observed at 1405 cm^{-1} . The bimetallic complex has intense peaks at 1625 and 1600 cm^{-1} that are assigned to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$, with the same limitations as described earlier. The ring vibrations are at 1422 cm^{-1} . While exact assignments are elusive, the overall trend of increasing frequencies upon addition of the electron-withdrawing RhCl_3 group is clear.

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