Corp. for support of this work. We also acknowledge the NSF for providing funds that facilitated the purchase of the FT IR spectrometer and the TT-14 FT NMR spectrometer.

Registry No. [Rh(PPh$_3$)$_2$(CO)(Guo)]PF$_6$, 84049-95-6; [Rh(PPh$_3$)$_2$(CO)(Ino)]PF$_6$, 84049-97-8; [Rh(PPh$_3$)$_2$(CO)(1-MeIno)]PF$_6$, 84056-86-0; [Rh(PPh$_3$)$_2$(CO)(Ado)]PF$_6$, 84049-99-0; [Rh(PPh$_3$)$_2$(CO)(Pur)]PF$_6$, 84050-01-1; [Rh(PPh$_3$)$_2$(CO)(Ade)]PF$_6$, 84050-03-3; [Rh(PPh$_3$)$_2$(CO)(cyclohexanone)]PF$_6$, 84050-05-5; [Rh(PPh$_3$)$_2$(CO)$_3$]PF$_6$, 53433-43-5.

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Chemistry of Ruthenium. 7.[1] Aquo Complexes of Isomeric Bis[2-(arylazo)pyridine]ruthenium(II) Moieties and Their Reactions: Solvolysis, Protic Equilibria, and Electrochemistry

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The two blue isomers of RuCl$_2$L$_2$ are trans,cis (**2**) and cis,cis (**3**) in the following sequence: N(pyridine), N(pyridine); N(azo), N(azo) [L = 2-(phenylazo)pyridine (pap) or 2-(*m*-tolylazo)pyridine (tap)]. Both **2** and **3** undergo facile and stereoretentive displacement of Cl$^-$ by H$_2$O in the presence of aqueous Ag$^+$, affording the corresponding isomers **5** and **6** of Ru(OH$_2$)$_2$L$_2$$^{2+}$ (isolated as the perchlorate hydrate). Conversely, **5** and **6** regenerate **2** and **3**, respectively, in chloride media. Deprotonation of **5** (L = pap; pK_1 = 6.80, pK_2 = 8.66) affords Ru(OH)(OH$_2$)(pap)$_2$$^+$ (**8**) and Ru(OH)$_2$(pap)$_2$ (**9**), both of which have been isolated in the pure form (the former as a perchlorate salt). The $t_{2g} \rightarrow \pi^*$(L) MLCT transition energies as well as the N=N stretching frequencies decrease on deprotonation (**5** > **8** > **9**) due to t_{2g}–p(OH$^-$) and t_{2g}–π^*(L) interactions. Both **5** and **6** (but not **8** and **9**) undergo stereoretentive solvolysis in donor solvents (S), furnishing RuS$_2$L$_2$$^{2+}$, of which one, viz., Ru(PhCN)$_2$(tap)$_2$$^{2+}$, is isolated as a crystalline perchlorate. Reaction of **5** (L = pap) with pyridine (py) and subsequent acidification and processing furnishes the perchlorate salt of the monobasic acid (pK_1 = 6.80) Ru(OH$_2$)(py)(pap)$_2$$^{2+}$ (**7**). The pK values of **5** and **7** reflect the strong π acidity of L. The consequent stability of the t_{2g} level in turn leads to high redox potentials in Ru–L complexes. Complexes **8** (in MeCN) and **9** (in CH$_2$Cl$_2$) display quasi-reversible Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples: $8^{2+} + e^- \rightleftharpoons 8^+$, $8^+ + e^- \rightleftharpoons 8$; $9^{2+} + e^- \rightleftharpoons 9^+$, $9^+ + e^- \rightleftharpoons 9$. The respective $E°_{298}$ values are as follows: 1.18, 1.89 V; 1.07, 1.53 V (vs. SCE). For **7** (in MeCN) the couple $7^+ + e^- \rightleftharpoons 7$ is observed ($E°_{298}$ = 1.5 V) initially but it is rapidly replaced by a couple with $E°_{298}$ of 1.88 V due to solvolysis. In acidic (pH 1–4) aqueous media the 2e$^-$–2H$^+$ couple Ru^{IV}(O)(py)(pap)$_2$$^{2+}$ + 2e$^-$ + 2H$^+$ $\rightleftharpoons$ **7** occurs ($E°_{298}$ = 1.20 V).

Introduction

Well-characterized aquo complexes of ruthenium(II) that have been isolated in the crystalline state are relatively uncommon.[2-8] Such species are potential starting materials for making a variety of ruthenium–ligand bonds by the nucleophilic displacement reactions (1) and (2), where D and D$^-$ are

$$(\mathrm{Ru{-}OH_2})^{2+} + \mathrm{D} \rightarrow (\mathrm{Ru{-}D})^{2+} + \mathrm{H_2O} \qquad (1)$$

$$(\mathrm{Ru{-}OH_2})^{2+} + \mathrm{D^-} \rightarrow (\mathrm{Ru{-}D})^{+} + \mathrm{H_2O} \qquad (2)$$

respectively neutral or anionic ligands. Simple deprotonation, straightforward electron loss, and a coupling of the two in oxidative proton loss constitute yet other reaction possibilities (eq 3–6).

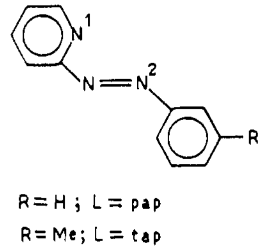
$$(\mathrm{Ru{-}OH_2})^{2+} \rightarrow (\mathrm{Ru{-}OH})^{+} + \mathrm{H^+} \qquad (3)$$

$$(\mathrm{Ru{-}OH_2})^{2+} \rightarrow (\mathrm{Ru^{III}{-}OH_2})^{3+} + e^- \qquad (4)$$

$$(\mathrm{Ru{-}OH_2})^{2+} \rightarrow (\mathrm{Ru^{III}{-}OH})^{2+} + \mathrm{H^+} + e^- \qquad (5)$$

$$(\mathrm{Ru{-}OH_2})^{2+} \rightarrow (\mathrm{Ru^{IV}{=}O})^{2+} + 2\mathrm{H^+} + 2e^- \qquad (6)$$

We have shown[9,10] that the bidentate azopyridine ligand L (**1**) imparts excellent stability to ruthenium(II). It was therefore considered logical that the mixed species with L and H$_2$O as coligands should be stable enough for ready isolation in the pure state. Herein we report the synthesis and characterization of two isomeric forms of the diaquo species [Ru(OH$_2$)$_2$L$_2$](ClO$_4$)$_2$·H$_2$O and of the monoaquo complex [Ru(OH$_2$)(py)L$_2$](ClO$_4$)$_2$·H$_2$O (py = pyridine). Selected reactions belonging to types 1–6 are described for one of the diaquo isomers as well as for the monoaquo complex. Where appropriate, the results are compared with those of Ru–bpy species (bpy = 2,2′-bipyridine).



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While L is the general abbreviation for the azopyridine ligands, the two specific ligands concerning us here, viz., 2-(phenylazo)pyridine and 2-(*m*-tolylazo)pyridine are respectively abbreviated as pap and tap.

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(10) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 2737.

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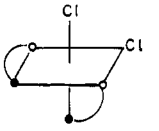
Table I. Selected Infrared, Molar Conductivity, and Analytical Data

compd	IR[a,b] ν_{max}, cm^{-1} C=N	IR[a,b] ν_{max}, cm^{-1} N=N	molar conductivity solvent	molar conductivity Λ, Ω^{-1} cm^2 M^{-1}	anal. data[c] % C	anal. data[c] % H	anal. data[c] % N
tc-$[Ru(OH_2)_2(pap)_2](ClO_4)_2 \cdot H_2O$[d]	1600	1325	H_2O CH_3CN	240 300	36.87 (36.66)	3.00 (3.33)	11.42 (11.66)
tc-$[Ru(OH_2)_2(tap)_2](ClO_4)_2 \cdot H_2O$	1600	1320	H_2O CH_3CN	240 305	38.24 (38.49)	3.52 (3.74)	11.02 (11.22)
cc-$[Ru(OH_2)_2(tap)_2](ClO_4)_2 \cdot H_2O$	1595	1315	H_2O CH_3CN	245 340	38.44 (38.49)	3.23 (3.74)	11.12 (11.22)
tc-$[Ru(OH)(OH_2)(pap)_2](ClO_4) \cdot H_2O$	1590	1295	CH_3CN	145	42.81 (42.60)	3.38 (3.71)	13.37 (13.55)
tc-$Ru(OH)_2(pap)_2 \cdot H_2O$	1600	1285	CH_3CN	12	50.93 (50.85)	4.66 (4.23)	15.85 (16.18)
tc-$[Ru(C_6H_5CN)_2(tap)_2](ClO_4)_2$	1600	1355	CH_3CN	305	50.07 (50.66)	3.06 (3.56)	12.68 (12.44)
tc-$[Ru(OH_2)(py)(pap)_2](ClO_4)_2 \cdot H_2O$	1600	1335	H_2O CH_3CN	230 320	41.21 (41.48)	3.47 (3.46)	12.49 (12.55)
tc-$[Ru(OH_2)(pic)(pap)_2](ClO_4)_2 \cdot H_2O$	1590	1330	CH_3CN	325	41.92 (42.25)	3.52 (3.65)	12.05 (12.32)

[a] All bands are sharp and strong. [b] In KBr disk (4000–400 cm^{-1}). [c] Calculated values are in parentheses. [d] Analytical data for Cl: 9.92 (9.85).

Results and Discussion

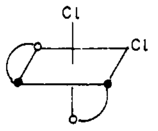
Structure of Starting Materials and the Synthetic Reaction. Both $RuCl_2(pap)_2$ and $RuCl_2(tap)_2$ exist in three isomeric forms,[9-11] two being blue and the third green. The structures of the two blue isomers (**2** and **3**) of $RuCl_2(pap)_2$ are now accurately known[12] from three-dimensional X-ray work. Both have the *cis*-$RuCl_2$ moiety. Isomer stereochemistry is best defined by considering the relative positions in the pair N^1, N^1 and in the pair N^2, N^2 taken in that order and allowing chloride (or other donors, see later) to occupy the remaining two octahedral positions.[12] In one of the blue isomers (**2**), N^1, N^1 span trans positions and N^2, N^2 cis positions. This isomer is called trans–cis or simply *tc*. The other blue isomer (**3**) is cis–cis (*cc*). The cis–trans isomer (*ct*) also based on *cis*-$RuCl_2$ is possible in principle,[10] but there is no evidence for its existence. The two blue isomers of $RuCl_2(tap)_2$ are logically assumed[13] to be *tc* and *cc*. The green isomer of $RuCl_2L_2$ has a *trans*-$RuCl_2$ configuration, and its gross geometry as based on convincing chemical and spectroscopic considerations[9,11] is trans–trans (*tt*), **4**.



tc

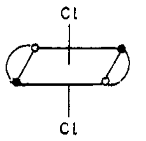
2

○ N^1
● N^2



cc

3



tt

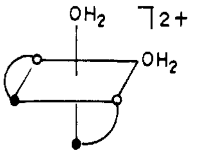
4

The isomers of $RuCl_2L_2$ were used as the starting materials for the synthesis of aquo species. Silver(I)-assisted halide displacement[14,15] (eq 7) proceeds smoothly and in good yield

$$RuCl_2L_2 + 2Ag^+ \xrightarrow{H_2O} Ru(OH_2)_2L_2{}^{2+} + 2AgCl \quad (7)$$

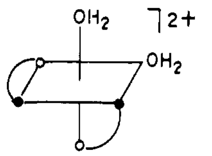
for both *tc* (**2**) and *cc* (**3**) complexes in aqueous media. The *tt* isomer (**4**) is unreactive[9,10] toward silver(I).

Two Diaquo Isomers and Their Stereochemistry. The diaquo cation is isolated in the crystalline state as the dark-colored perchlorate salt, $[Ru(OH_2)_2L_2](ClO_4)_2 \cdot H_2O$. The salt obtained from the *tc* isomer is different from that obtained from the *cc* isomer. The difference lies in cation isomerism. Both salts behave as 1:2 electrolytes in acetonitrile and water (Table I). The stereochemistries of the isomeric cations were established with use of ^1H NMR data. In dimethyl-d_6 sulfoxide[16] the isomer of $Ru(OH_2)_2(tap)_2{}^{2+}$ derived from *tc*-$RuCl_2(tap)_2$ shows a single sharp methyl signal at 2.14 ppm whereas the other isomer derived from *cc*-$RuCl_2(tap)_2$ shows two equally intense methyl signals at 2.16 and 2.36 ppm. Thus the RuL_2 fragment of the diaquo species retains the symmetry of the dihalo precursors.[13] The coordination spheres of the diaquo isomers are then **5** and **6**, respectively. This assertion is further strengthened by the products of anation of **5** and **6**. In aqueous solution chloride ions regenerate **2** and **3**, re-



tc

5



cc

6

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(11) Krause, R. A.; Krause, K. *Inorg. Chem.* **1980**, *19*, 2600.

(12) Seal, A.; Ray, S., to be submitted for publication. (The *tc* complex is monoclinic, $P2_1/c$ with $Z = 4$. At the present level of refinement ($R = 0.051$) average distances in the coordination octahedron are as follows: Ru–Cl, 2.399; Ru–N^1, 2.049; Ru–N^2, 1.980 Å. The *cc* isomer is triclnic ($P\bar{1}$). The average distances ($R = 0.054$) in the coordination octahedra of two independent complexes are as follows: Ru–Cl, 2.40; Ru–N^1, 2.05; Ru–N^2, 1.97 Å. It is significant that in both complexes Ru–N^2 bonds are shorter than the Ru–N^1 bonds. In both *tc* and *cc* isomers the N^1–Ru–N^2 angles are close to 76° whereas Cl–Ru–Cl angles lie within 1° of 91.5°. X-ray work on *tt*-$RuCl_2(pap)_2$ is in progress. In an earlier paper[10] an isomer description was made considering all three coordinating pairs: Cl, Cl; N^1, N^1; N^2, N^2. Thus the *tc* complex was called *ctc* and so on. Since chloride positions are automatically fixed by the RuL_2 stereochemsitry, the shorter descriptions are sufficient for stereochemical definition.)

(13) The *tc* and *cc* isomers are readily distinguished[9-11] by their metal to ligand charge-transfer band maxima at ~580 and ~570 nm, respectively. In the case of $RuCl_2(tap)_2$ ^1H NMR (δ_{Me}) in $CDCl_3$ is useful: *tc*, 2.14; *cc*, 2.13 and 2.33.

(14) In the case[15] of *cis*-$RuCl_2(bpy)_2$ similar halide displacement by Ag^+ has been used to generate solvent species in solution. However, this reaction has not been utilized for the synthesis of salts of *cis*-$Ru(OH_2)_2(bpy)_2{}^{2+}$. Such salts are made[6] in poor yield by reacting $Ru(CO_3)(bpy)_2$ with aqueous HPF_6.

(15) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(16) As discussed later in the text, in donor solvents the coordinated water molecules are displaced by solvent molecules. In $(CD_3)_2SO$, the species being looked at is essentially $Ru((CD_3)_2SO)_2(tap)_2{}^{2+}$. The ^1H NMR spectral results and the results on anation in aqueous solution (eq 8 of the text) show that solvolysis as well as anation proceeds with retention of configuration of the RuL_2 fragment.

Table II. Visible–Ultraviolet Spectral Data

compd	solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
tc-$[Ru(OH_2)_2(pap)_2](ClO_4)_2 \cdot H_2O$	1 M aq H_2SO_4	538 (11 270), 364 (14 825), 300 (16 485)
	CH_3CN^a	500 (9850), 476^e (6820), 364 (17 220), 308^e (12 075), 280 (16 880), 218 (22 600)
	$HCON(CH_3)_2{}^a$	568 (12 240), 364^e (16 700), 318 (23 920)
	$(CH_3)_2SO^a$	560 (12 020), 362^e (17 250), 312 (21 600)
tc-$[Ru(OH_2)_2(tap)_2](ClO_4)_2 \cdot H_2O$	1 M aq H_2SO_4	536 (11 400), 366 (15 250), 308^e (15 090), 290 (16 450)
	CH_3CN^a	500 (10 160), 476^e (7050), 368 (17 650), 308^e (13 300), 280 (17 780), 216 (25 400)
cc-$[Ru(OH_2)_2(tap)_2](ClO_4)_2 \cdot H_2O$	1 M aq H_2SO_4	518 (10 060), 364 (14 900), 308^e (12 250), 274 (13 575)
	CH_3CN^a	492 (8850), 366 (15 950), 274 (14 550), 216 (23 300)
tc-$[Ru(OH)(OH_2)(pap)_2]ClO_4 \cdot H_2O$	aq (80:20) dioxane (pH 7.8)	550 (9640), 368^e (14 600), 316 (19 200)
	CH_3CN	550 (8480), 460^e (2700), 360^e (14 700), 318 (19 900), 218 (25 780)
tc-$Ru(OH)_2(pap)_2$	CH_2Cl_2	580 (10 700), 372^e (2650), 322 (20 200), 232 (21 650),
tc-$[Ru(C_6H_5CN)_2(tap)_2](ClO_4)_2$	C_6H_5CN	500 (7500), 362 (16 400)
tc-$[Ru(OH_2)(py)(pap)_2](ClO_4)_2 \cdot H_2O$	1 M aq H_2SO_4	530 (11 190), 386 (18 750), 310^e (16 500), 288 (17 850)
	aq NaOH soln (pH 10)^b	562 (9850), 454^e (2950), 360^e (18 300), 306 (21 850)
	CH_3CN^c	510 (10 400), 484^e (7480), 368 (19 450), 310 (17 450), 284 (19 450), 218 (25 580)
tc-$[Ru(OH_2)(pic)(pap)_2](ClO_4)_2 \cdot H_2O$	1 M aq H_2SO_4	530 (12 100), 388 (19 500), 304^e (17 200), 286 (19 280)
	CH_3CN^d	510 (11 700), 484^e (9200), 368 (21 400), 308^e (18 800), 284 (21 500), 218 (29 550)

[a] Due to solvolysis the observed spectra are those of $RuS_2L_2{}^{2+}$. [b] At this pH, the observed spectrum is of $Ru(OH)(py)(pap)_2{}^+$. [c] Due to solvolysis the observed spectrum is that of $Ru(CH_3CN)(py)(pap)_2{}^{2+}$. [d] Due to solvolysis the observed spectrum is that of $Ru(CH_3CN)(pic)(pap)_2{}^{2+}$. [e] Shoulder.

spectively, from **5** and **6** quantitatively,[17] $RuCl_2L_2$ being insoluble in water precipitates. Thus we have the stereoretentive interconversion scheme (8). As in the case of $RuCl_2L_2$, the two diaquo isomers **5** and **6** will be called *tc* and *cc* isomers, respectively.

$$\mathbf{2}\ (\mathbf{3}) \underset{Cl^-,\ H_2O}{\overset{Ag^+,\ H_2O}{\rightleftharpoons}} \mathbf{5}\ (\mathbf{6}) \qquad (8)$$

The infrared spectra (Table I) of the perchlorates of **5** and **6** are closely alike: $\nu_{N=N}$, ~1330; $\nu_{C=N}$, ~1600; ν_{H_2O}, ~3400; $\nu_{ClO_4^-}$, ~1100 and 620 cm^{-1}. Like the dihalo species,[9-11] the diaquo complexes display (Table II, Figure 1) metal to ligand charge-transfer (MLCT) transitions of the type $Ru(t_{2g}) \rightarrow L(\pi^*)$ in the visible region. The MLCT band maxima of **5** and **6** occur respectively at 536 and 518 nm (Table II, Figure 1). The former is more intense than the latter. The same trends of band energy and intensity apply[13] to the *tc* and *cc* isomers of $RuCl_2L_2$. The MLCT band is blue shifted in going from $RuCl_2L_2$ to $Ru(OH_2)_2L_2{}^{2+}$ for the *tc* pair as well as for the *cc* pair. The *Dq* order $H_2O > Cl^-$ resulting in better stabilization of the t_{2g} level in the diaquo species could be responsible for this shift.

Solvolysis of $Ru(OH_2)_2L_2{}^{2+}$. On dissolution of the *tc* isomer in donor solvents (S), the MLCT band energy undergoes significant shifts from acidic aqueous solution values (Table II) due to substitution of coordinated water by solvent molecules. In acetonitrile and benzonitrile the shifts are hypsochromic as expected from the *Dq* order $RCN > H_2O$. From benzonitrile solution, the yellow-orange adduct $[Ru(PhCN)_2(tap)_2](ClO_4)_2$ has been isolated in the crystalline state. It shows two C≡N stretches at 2250 and 2220 cm^{-1} as expected[18] for the cis structure of the $Ru(PhCN)_2$ moiety (PhCN displacing H_2O in **5**). There is good reason[16] to believe that the solvolysis reaction is stereoretentive (eq 9).

$$tc\text{-}Ru(OH_2)_2L_2{}^{2+} + 2S \rightarrow tc\text{-}RuS_2L_2{}^{2+} + 2H_2O \qquad (9)$$

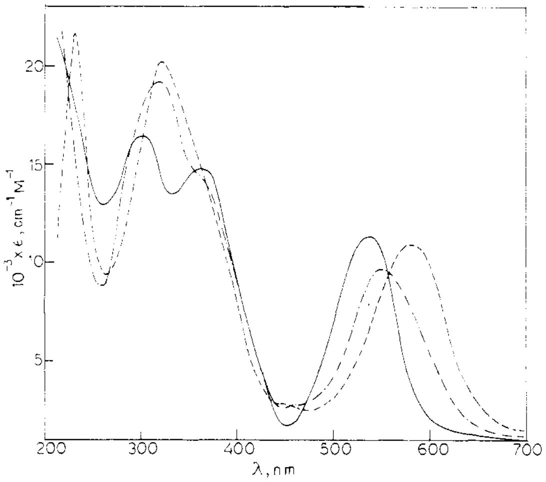

Figure 1. Electronic spectra of (—) *tc*-$[Ru(OH_2)_2(pap)_2](ClO_4)_2 \cdot H_2O$, (–·–·) *tc*-$[Ru(OH)(OH_2)(pap)_2]ClO_4 \cdot H_2O$, and (- - -) *tc*-$Ru(OH)_2(pap)_2 \cdot H_2O$ in 1 M aqueous sulfuric acid, an 80:20 water–dioxane mixture (pH 7.8), and CH_2Cl_2, respectively.

Preliminary studies have shown that *cc*-$Ru(OH_2)_2L_2{}^{2+}$ behaves in a manner similar to that of the *tc* isomer. In acetonitrile the MLCT band position is blue shifted (Table II) due to formation of *cc*-$Ru(MeCN)_2L_2{}^{2+}$. The energy order *cc* > *tc* for the MLCT band is again[13] obeyed.

Reaction of *tc*-$Ru(OH_2)_2(pap)_2{}^{2+}$ with Pyridine Bases. Pyridine acts as a base and as a ligand toward the diaquo species. The facile reaction (10) occurs at room temperature[19]

$$Ru(OH_2)_2(pap)_2{}^{2+} + py \rightarrow Ru(OH)(py)(pap)_2{}^+ + pyH^+ + H_2O \qquad (10)$$

in both neat and aqueous pyridine. Excessive solubility has precluded the isolation of the blue-violet cation $Ru(OH)(py)(pap)_2{}^+$ as a crystalline salt. However, acidification of

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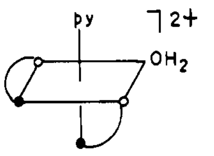
[17] The IR and UV-vis spectra of compounds obtained by anation of **5** and **6** with Cl^- are indistinguishable from those of authentic[9,11] **2** and **3**, respectively.

[18] Davis, J. A.; Heartley, F. R.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2246.

[19] Under forcing conditions (in boiling aqueous pyridine) crystals of the disubstituted product $[Ru(py)_2(pap)_2](ClO_4)_2$ were isolated. The complex is a 1:2 electrolyte in MeCN and shows an MLCT transition at 530 nm in the same solvent.

the reaction mixture yields red $Ru(OH_2)(py)(pap)_2^{2+}$ (**7**), which occurs in the salt $[Ru(OH_2)(py)(pap)_2](ClO_4)_2 \cdot H_2O$ (Tables I and II).



tc

7

Pyridine also converts $Ru(OH)(OH_2)(pap)_2^+$ (see below) to $Ru(OH)(py)(pap)_2^+$ (eq 11), suggesting that the former

$$Ru(OH)(OH_2)(pap)_2^+ + py \rightarrow Ru(OH)(py)(pap)_2^+ + H_2O \quad (11)$$

cation may be an intermediate in reaction 10. The behavior of β-picoline (pic) is entirely analogous to that of pyridine.

The RuL_2 stereochemistry is retained in deprotonation (see below) and solvolysis reactions. Reaction 10 is a combination of these types of reactions, and reaction 11 is mere solvolysis. Therefore, the RuL_2 stereochemsitry in $Ru(OH_2)(py)(pap)_2^{2+}$ is taken to be the same, i.e., *tc* (**7**), as that in the parent complex (**5**).

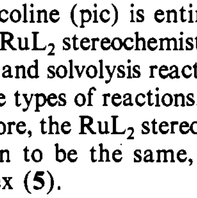
Protic Equilibria. (a) *tc*-$Ru(OH_2)_2(pap)_2^{2+}$. This dibasic acid can be titrated pH-metrically with sodium hydroxide solution in an 80:20 water–dioxane mixture. At 298 K the values of pK_1 and pK_2 are found to be 6.80 ± 0.05 and 8.66 ± 0.05, respectively.

Reactions 12 and 13 are perfectly reversible, and each of

$$Ru(OH_2)_2(pap)_2^{2+} \overset{K_1}{\rightleftharpoons} Ru(OH)(OH_2)(pap)_2^+ + H^+ \quad (12)$$

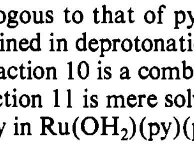
$$Ru(OH)(OH_2)(pap)_2^+ \overset{K_2}{\rightleftharpoons} Ru(OH)_2(pap)_2 + H^+ \quad (13)$$

three species involved in the equilibria can be converted to any one of the other two merely by adjustment of pH at ambient temperature. Since peripheral proton transfer is the key step in such conversions, the gross RuL_2 stereochemistry is taken to be the same for all the three species (type **5**). We thus have *tc*-$Ru(OH)(OH_2)(pap)_2^+$ (**8**) and *tc*-$Ru(OH)_2(pap)_2$ (**9**). The former is isolated as a blue-violet perchlorate hydrate and the latter as a blue hydrate. This hydrate rapidly reverts to **8** in a moist environment. We note that crystalline species of type **9** are virtually unknown in bivalent ruthenium chemistry. Further, **8** represents a rare type.[2,6]



tc

8



tc

9

As the pH of an aqueous solution of *tc*-$Ru(OH_2)_2(pap)_2^{2+}$ is varied from 4.5 to 12.0, the MLCT band is progressively red shifted from 536 nm (pure **5** (L = pap)) to 580 nm (pure **9**). In **8** the band is at 550 nm (Table II). Hydroxo coordination can[5] destabilize the t_{2g} level of ruthenium via a p-(OH^-)–$t_{2g}(Ru)$ interaction, thus decreasing the energy of the MLCT band. In this context it is significant that the N=N stretching frequencies (Table I) follow the order diaquo > hydroxoaquo > dihydroxo. The N=N frequencies in complexes of the RuL_2^{2+} moiety are relatively low compared to free ligand values due to $t_{2g} \rightarrow \pi^*$(azo) donation.[10,11] The extent of this donation would increase and the N=N frequency would decrease as the t_{2g} level gets destabilized. This explains the observed order of frequencies noted above. The trends in N=N frequencies and MLCT band energies are mutually consistent.

Unlike in *tc*-$Ru(OH_2)_2(pap)_2^{2+}$, the Ru–OH_2 bond in **8** is not solvolyzed in acetonitrile. The MLCT band remains unaffected (550 nm) in going from aqueous dioxane to acetonitrile solution (Table II). Intramolecular hydrogen bonding between aquo and hydroxo groups may have a role[20] in bringing about the decrease in aquo lability.

(b) *tc*-$Ru(OH_2)(py)(pap)_2^{2+}$ (7). The pK of this acid is 6.80 ± 0.05 in aqueous solution (eq 14). It is instructive to compare the pK of **7** with those of other monoaquo ruthenium(II) species:

$$Ru(OH_2)(py)(pap)_2^{2+} \overset{K}{\rightleftharpoons} Ru(OH)(py)(pap)_2^+ + H^+ \quad (14)$$

$Ru(OH_2)(NH_3)_5^{2+}$ (pK = 12.3,[4] 13.1[2]); *cis*-$Ru(OH_2)(py)(bpy)_2^{2+}$ (pK = 10.26[5]). Thus **7** is the strongest acid in this series. In particular, the substitution of two bpy with two pap ligands brings about a dramatic augmentation of acidity. This is attributed to the much stronger π-acceptor character of pap compared to that of bpy. The $Ru \leftarrow OH_2$ σ bond is correspondingly stronger in the pap complex, resulting in easier proton dissociation. It is probably because of the strong π-acidity character of the pap ligand that the replacement of H_2O by py hardly affects the pK values. The pK_1 values of **5** (L = pap) and **7** are the same.

The variable-pH MLCT spectra of **7** were studied. The band position shifts from 530 nm (pure **7**) in acidic media to 562 nm (pure *tc*-$Ru(OH)(py)(pap)_2^+$) in basic media with an isosbestic point at 552 nm.

Electrochemical Redox Equilibria. All measurements were performed with use of platinum as the working electrode. Sodium perchlorate (aqueous solution) and tetraethylammonium perchlorate (nonaqueous solution) were used as supporting electrolytes. All potentials are referenced to the saturated calomel electrode (SCE). Voltammetric data are in Table III. Several one-electron quasi-reversible responses seen at negative potentials primarily involve[9,10] ligand reduction. These will not be considered any further in this work.

(a) *tc*-$Ru(OH_2)_2L_2^{2+}$ (5), *tc*-$Ru(OH)(OH_2)(pap)_2^+$ (8), and *tc*-$Ru(OH)_2(pap)_2$ (9). Complexes of the RuL_2^{2+} radical are known to display a reversible to quasi-reversible ruthenium(III)/ruthenium(II) couple at relatively high positive potential[9-11] (2.08–0.9 V) attainable only in nonaqueous solvents. This is in full agreement with the high stability of the t_{2g} level arising from the strong π acidity of L. Accordingly, *tc*-$Ru(OH_2)_2L_2^{2+}$ and its two deprotonated derivatives display no voltammetric oxidative response in aqueous solution up to the onset of solvent oxidation (~1 V in acidic media). It is possible to estimate[21,22] that $E°_{298}$ of the couple (15) is ~1.5

$$Ru^{III}(OH_2)_2L_2^{3+} + e^- \rightleftharpoons Ru^{II}(OH_2)_2L_2^{2+} \quad (15)$$

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(20) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J.; Peedin, J. *Inorg. Chem.* **1979**, *18*, 3369.

(21) On the basis of reported data[9,10] and our unpublished results[22] it is estimated that the replacement of one bpy by one pap in ruthenium(II) complexes shifts the $E°_{298}$ value of the ruthenium(III)/ruthenium(II) couple by 300 ± 100 mV. Since the $E°_{298}$ of *cis*-$Ru(OH_2)_2(bpy)_2^{2+}$ is 0.63 V[7] in aqueous acidic solution, the $E°_{298}$ of *tc*-$Ru(OH_2)_2(pap)_2^{2+}$ in a similar solution is estimated to be ~1.2 V. On the other hand, with use of the $E°_{298}$–ν(MLCT) correlation curve[10] and the experimental value (18 700 cm^{-1}) of ν(MLCT) of *tc*-$Ru(OH_2)_2(pap)_2^{2+}$, the $E°_{298}$ is computed to be ~1.5 V.

(22) Some representative $E°_{298}$ values are as follows: $Ru(bpy)_3^{2+}$, 1.29 V; $Ru(bpy)_2(pap)^{2+}$, 1.60 V; $Ru(bpy)(pap)_2^{2+}$, 1.89 V; $Ru(pap)_3^{2+}$, 2.22 V.

Table III. Electrochemical Data[a,b] at a Platinum Electrode (298 K)

compd	$E°_{298}$, V (ΔE_p, mV)	
	metal-centered oxidn	ligand-based redn
tc-$[Ru(OH_2)_2(pap)_2](ClO_4)_2 \cdot H_2O$	*c, d*	0.36 (110), 0.78 (120), 1.55 (100)
tc-$[Ru(OH_2)_2(tap)_2](ClO_4)_2 \cdot H_2O$	*c, d*	0.36 (110), 0.77 (130), 1.55 (90)
cc-$[Ru(OH_2)_2(tap)_2](ClO_4)_2 \cdot H_2O$	*c, d*	0.37 (140), 0.73 (130), 1.57 (90)
tc-$[Ru(OH)(OH_2)(pap)_2]ClO_4 \cdot H_2O$	1.18 (150), 1.89 (210)	0.58 (80), 1.11 (100), 1.66 (140)
tc-$Ru(OH)_2(pap)_2 \cdot H_2O$	1.07[e] (150), 1.53[e] (130)	0.58[e] (360), 1.19[e] (350)
tc-$[Ru(OH_2)(py)(pap)_2](ClO_4)_2 \cdot H_2O$	1.88 (100)[f]	0.32 (80), 0.78 (110), 1.55 (100), 1.74 (120)
tc-$[Ru(OH_2)(pic)(pap)_2](ClO_4)_2 \cdot H_2O$	1.88 (120)[f]	0.28 (80), 0.74 (110), 1.49 (100), 1.70 (140)

[a] Meaning of symbols is the same as in the text. [b] Unless otherwise stated, the solvent is acetonitrile (0.1 M in TEAP), the solute concentration is 10^{-3} M, and the scan rate is 50 mV s^{-1}. [c] Due to solvolysis the electroactive species is $Ru(CH_3CN)_2L_2^{2+}$. [d] No response is observed up to 2.0 V.[20,22] [e] Solvent is dichloromethane. [f] Due to solvolysis the electroactive complex has CH_3CN in place of H_2O. The response seen at 1.50 V immediately after dissolving the aquo complex is attributed to the latter; this response vanishes within a few minutes.

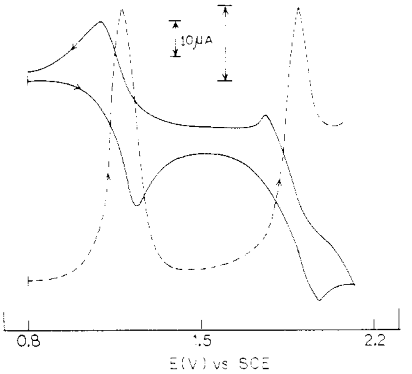

Figure 2. (—) Cyclic voltammogram of *tc*-$[Ru(OH)(OH_2)(pap)_2]ClO_4 \cdot H_2O$ in acetonitrile (0.1 M TEAP) at a platinum electrode with the scan rate 50 mV s^{-1} and (---) a differential pulse voltammogram at 5 mV s^{-1} scan rate and 25-mV modulation amplitude.

V. The electrochemical oxidative response of **5** remains equally elusive in nonaqueous solvent due to solvolysis. Thus in acetonitrile, *tc*-$Ru(MeCN)_2L_2^{2+}$ is formed, and this does not show oxidative response up to[23] 2.0 V.

Since **8** and **9** retain their identity in nonaqueous media, their cyclic and differential pulse voltammograms could be recorded in acetonitrile. The voltammograms of *tc*-$Ru(OH)(OH_2)(pap)_2^+$ are in Figure 2. The two quasi-reversible one-electron[24,25] couples having peak-to-peak separation (ΔE_p) in the range 150–250 mV (Table III) are (16) and (17). The

$$Ru^{III}(OH)(OH_2)(pap)_2^{2+} + e^- \rightleftharpoons Ru^{II}(OH)(OH_2)(pap)_2^+ \quad (16)$$

$$Ru^{IV}(OH)(OH_2)(pap)_2^{3+} + e^- \rightleftharpoons Ru^{III}(OH)(OH_2)(pap)_2^{2+} \quad (17)$$

formal potentials, $E°_{298}$ (taken as the average of peak potentials), of the couples are 1.18 and 1.89 V, respectively. The complex **9** is best studied in dichloromethane. Two quasi-reversible cyclics are again observed with formal potentials at 1.07 and 1.53 V corresponding to the couples (18) and (19).

$$Ru^{III}(OH)_2(pap)_2^+ + e^- \rightleftharpoons Ru^{II}(OH)_2(pap)_2 \quad (18)$$

$$Ru^{IV}(OH)_2(pap)_2^{2+} + e^- \rightleftharpoons Ru^{III}(OH)_2(pap)_2^+ \quad (19)$$

Table IV. Cyclic Voltammetric Data[a,b] of *tc*-$[Ru(OH_2)(py)(pap)_2](ClO_4)_2 \cdot H_2O$ in Aqueous Solution at 298 K

pH	$\bar{E}_p$, V (ΔE_p, mV)	$\Delta\bar{E}_p/\Delta$(pH), mV	$E°_{298}$, V
1.05	1.14 (35)		1.20
2.05	1.08 (35)	60	1.20
2.40	1.06 (30)	58	1.20
3.05	1.02 (35)	62	1.20
4.05	0.96 (40)	60	1.20

[a] Meaning of symbols is as in text; $\Delta\bar{E}_p/\Delta$(pH) represents the shift of $\bar{E}_p$ for a unit change of pH calculated from adjacent pairs of pH and $\bar{E}_p$ values. The supporting electrolyte is $NaClO_4$ (0.1 M), and the solute concentration is 9.1×10^{-5} M. [b] Scan rate 20 mV s^{-1}.

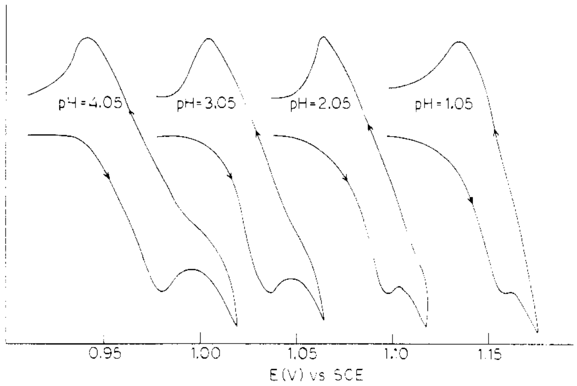

Figure 3. Cyclic voltammograms of *tc*-$[Ru(OH_2)(py)(pap)_2](ClO_4)_2 \cdot H_2O$ in water (0.1 M $NaClO_4$) at different pHs at a platinum working electrode.

(b) *tc*-$Ru(OH_2)(py)(pap)_2^{2+}$ (7). We first consider the results in acetonitrile solutions. Fresh solutions of **7** in this solvent show a one-electron cyclic response with $E°_{298}$ = 1.5 V[26] corresponding to the couple (20). With time the response

$$Ru^{III}(OH_2)(py)(pap)_2^{3+} + e^- \rightleftharpoons Ru^{II}(OH_2)(py)(pap)_2^{2+} \quad (20)$$

due to couple 20 diminishes and a new response appears at 190 V (Table III) with a corresponding shift of the MLCT band from 530 to 510 nm. We believe that the couple at 1.90 V corresponds to half-reaction 21, where *tc*-Ru(MeCN)-

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(23) The $E°_{298}$ of *cis*-$Ru(MeCN)_2(bpy)_2^{2+}$ is 1.44 V.[20] Hence[21] the corresponding value of the pap analogue should be ~2.0 V. From the $E°_{298}$–ν(MLCT) correlation[11] the $E°_{298}$ is again estimated as ~2.0 V. Experimental results show that the actual value of $E°_{298}$ is above 2.0 V.

(24) With the electrode used by us, the current height at a 50 mV s^{-1} scan rate and at a solute concentration of 1×10^{-3} M is 35–40 μA for a typical one-electron couple.[9,10] The current heights in couples (16) and (17), under similar conditions, fall in the same range.

(25) Mukherjee, R. N.; Rajan, O. A.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 785.

(26) The p*K* order *tc*-$Ru(OH_2)(py)(pap)_2^{2+}$ < *cis*-$Ru(OH_2)(py)(bpy)_2^{2+}$ < $Ru(OH_2)(NH_3)_5^{2+}$ was attributed to the strong π-acceptor character of pap. This also implies superior stability of the t_{2g} level in the pap complex. Correspondingly the $E°_{298}$ values of the ruthenium(III)/ruthenium(II) couples follow the order *tc*-$Ru(OH_2)(py)(pap)_2^{2+}$ > *cis*-$Ru(OH_2)(py)(bpy)_2^{2+}$ (0.78 V[5]) > $Ru(OH_2)(NH_3)_5^{2+}$ (−0.17 V[3]). The trends of p*K* and $E°_{298}$ values are thus internally consistent.

$(py)(pap)_2^{2+}$ is formed[27] by the displacement of water by MeCN in **7**.

$$\mathrm{Ru^{III}(MeCN)(py)(pap)_2^{3+} + e^- \rightleftharpoons Ru^{II}(MeCN)(py)(pap)_2^{2+}} \quad (21)$$

More interesting is the electrochemical behavior of **7** in aqueous solution. In strongly acidic media (pH 1.0–4.0) a cyclic response with peak-to-peak separation (ΔE_p) of 30–40 mV is observed at slow scan rates. The ΔE_p value is suggestive of *a reversible single-step two-electron transfer process*. The current height[28,29] also corresponds to a two-electron process and increases linearly with the square root of the scan rate. The average of the peak potentials shifts by 60 mV for a change of 1 pH unit (Table IV, Figure 3). The results are in agreement with the electrode reaction (22). The $E°_{298}$ of

$$\mathrm{Ru^{IV}(O)(py)(pap)_2^{2+} + 2e^- + 2H^+ \rightleftharpoons Ru^{II}(OH_2)(py)(pap)_2^{2+}} \quad (22)$$

$$E°_{298} = \bar{E}_p + 0.059\mathrm{pH} \quad (23)$$

the couple (22) can be written as[30] in eq 23, where $\bar{E}_p$ is the average of peak potentials. The $E°_{298}$ value is 1.20 V (Table IV).

For comparison we note that *cis*-$\mathrm{Ru(OH_2)(py)(bpy)_2^{2+}}$ undergoes[5] two separate one-electron transfers and the final product is the catalytically active complex[31] $\mathrm{Ru(O)(py)(bpy)_2^{2+}}$. In the pap complex a single two-electron, two-proton step is observed instead. This means that in the pap complex the ruthenium(III) intermediate undergoes spontaneous and quantitative disproportionation (eq 24). In effect the oxidation

$$2\mathrm{Ru(III)} \rightarrow \mathrm{Ru(II)} + \mathrm{Ru(IV)} \quad (24)$$

of ruthenium(III) to ruthenium(IV) occurs at a lower potential than the oxidation of ruthenium(II) to ruthenium(III). Such a situation can arise if a large proton-transfer contribution[30] occurs specifically[32] to the ruthenium(III)/ruthenium(II) couple at low pH. The behavior at higher pH values could be informative in this regard. Unfortunately, the voltammogram becomes progressively ill-defined at pH >4.

The species $\mathrm{Ru(O)(py)(pap)_2^{2+}}$ (eq 22) remains to be isolated as a salt.[33] When **5** reacts with excess cerium(IV) in 1 M perchloric acid, the MLCT band disappears only to reappear as time passes, eventually attaining the initial intensity.[34] The cycle can be repeated many times. We believe that cerium(IV) oxidizes **5** to $\mathrm{Ru^{IV}(O)(py)(pap)_2^{2+}}$, which is reconverted to **5** and water is catalytically oxidized to dioxygen (voltammetric observation of the dioxygen reduction wave). Studies on the $\mathrm{Ru^{IV}(O)}$ complex as a catalyst in various oxidation reactions are in progress.

Concluding Remarks

The crystalline perchlorate salts of the two isomers (**5** and **6**) of $\mathrm{Ru(OH_2)_2L_2^{2}+}$ constitute new examples of ruthenium aquo complexes. These are prepared from the corresponding dichloro species by stereoretentive halide displacement with $\mathrm{Ag^+}$. The third dichloro isomer (**4**) fails to react with silver(I). We note that all three isomers of $\mathrm{RuCl_2L_2}$ react with boiling aqueous sodium hydroxide, giving deep blue solutions that on acidification with perchloric acid turn red-violet and separate into an isomeric mixture of diaquo species. Further studies on the stereodynamic hydroxide reaction are on. The solvolysis of **5** and **6** to $\mathrm{RuS_2L_2^{2+}}$ occurs in donor solvents (S). The S molecules in $\mathrm{RuS_2L_2^{2+}}$ can be readily displaced to produce a variety of complexes of type $\mathrm{Ru(bidentate)L_2^{x+}}$ (x = 0, 1, or 2 depending on the charge of the bidentate ligand) including $\mathrm{RuL_3^{2+}}$, which are not[9,11] directly obtainable from $\mathrm{RuCl_3 \cdot 3H_2O}$. The rich chemistry of such species as well as that of the bridged chelate $\mathrm{L_2Ru(bridge)RuL_2^{y+}}$ (also obtained from the diaquo parent) will be reported separately. The present results further demonstrate that the ruthenium chemistry of the 2-(arylazo)pyridine ligand is extensive. In the $\mathrm{RuL_2^{2+}}$ radical L has a stronger π-acceptor character than bpy in $\mathrm{Ru(bpy)_2^{2+}}$. In effect the t_{2g} level is more stable in complexes of L than in complexes of bpy. The systematically higher formal potentials of ruthenium(III)/ruthenium(II) couples and the higher acidity of the aquo complexes among chelates of L compared to those of bpy fall in place. The novel single-step two-electron, two-proton nature of the ruthenium(IV)/ruthenium(II) couple (22) is also related to the same phenomenon. The catalytic potential of the oxo complex may be considerable and is under further study.

Experimental Section

Materials. The isomeric $\mathrm{RuCl_2L_2}$ complexes were prepared by following reported methods.[9-11] Water of high purity was obtained by distillation of deionized water from $\mathrm{KMnO_4}$. Sodium perchlorate for electrochemical work was recrystallized from water. The purification of solvents and preparation of supporting electrolytes for electrochemical work were done as before.[10] Cerium(IV) solutions were prepared from reagent grade ceric sulfate, $\mathrm{Ce(SO_4)_2 \cdot 4H_2O}$. Dinitrogen was purified by bubbling it through an alkaline dithionite reducing solution. All other chemicals used for preparative works were of reagent grade and were used without further purification.

Measurements. Spectroscopic data were obtained with use of the following instruments: electronic spectra, Cary 17D or Pye Unicam SP8-150 spectrophotometer; IR spectra (KBr disk, 4000–400 $\mathrm{cm^{-1}}$), Beckman IR-20A spectrophotometer; ^{1}H NMR spectra (in $\mathrm{(CD_3)_2SO}$), Varian T-60A spectrometer. Voltammetric measurements were done with use of a PAR Model 370-4 electrochemistry system: Model 174A polarographic analyzer, Model 175 universal programmer, Model RE0074 XY recorder, Model 377A cell system. All experiments were done under a dinitrogen atmosphere in a three-electrode configuration using planar Beckman Model 39273 platinum as the working electrode. All results were collected at 298 K and are referenced to the saturated calomel electrode. The reported potentials are uncorrected for junction contributions.

Determination of p*K* Values. pH-metric titrations were done under a dinitrogen atmosphere on 10 mL of 5×10^{-3} M *tc*-$\mathrm{[Ru(OH_2)_2(pap)_2]}$

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(27) The possible formation of $\mathrm{Ru(MeCN)_2(pap)_2^{2+}}$ was considered. However, the spectral and electrochemical properties of the later species (already described in an earlier section of the text) are entirely different from those observed here.

(28) The current height in this case is 2.8 times higher than that observed[24] in case of a one-electron transfer process.

(29) Coulometric confirmation of a two-electron process is vitiated by the continuous count at the potential higher than the anodic peak potential (1.2 V).

(30) Mohanty, J. G.; Chakravorty, A. *Inorg. Chem.* **1976**, *15*, 2912; **1977**, *16*, 1561.

(31) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310. Moyer, B. A.; Meyer, T. J. *Ibid.* **1978**, *100*, 3601.

(32) For example, the couples could be

$$\mathrm{Ru^{IV}(O)(py)(pap)_2^{2+} + e^- \rightleftharpoons Ru^{III}(O)(py)(pap)_2^{+}}$$

$$\mathrm{Ru^{III}(O)(py)(pap)_2^{+} + e^- + 2H^+ \rightleftharpoons Ru^{II}(OH_2)(py)(pap)_2^{2+}}$$

At low pH the latter couple could conceivably "overtake" the former couple, making the observation of single-step transformation, ruthenium(IV) ⇌ ruthenium(II), possible.[30] Ruthenium(III)–oxo species implied in the above scheme ($\mathrm{Ru^{III}(O)(py)(pap)_2^{+}}$) are not documented in the literature. The ruthenium(III) complex $\mathrm{Ru(OH)(py)(bpy)_2^{2+}}$ does not deprotonate.[5] However, *tc*-$\mathrm{Ru(OH_2)(py)(pap)_2^{2+}}$ (p*K* = 6.80) is a much stronger acid than *cis*-$\mathrm{Ru(OH_2)(py)(bpy)_2^{2+}}$ (p*K* = 10.26[5]). The much-augmented acidity of the pap–aquo complex could make the oxo complex $\mathrm{Ru^{III}(O)(py)(pap)_2^{+}}$ a plausible intermediate.

(33) By the reaction of *tc*-$\mathrm{Ru(OH_2)(py)(pap)_2^{2+}}$ with a 10× excess of cerium(IV) in 1 M $\mathrm{H_2SO_4}$ a brown salt has been isolated from the yellow-orange reaction mixture after addition of excess sodium perchlorate. The compound is probably a hydrated perchlorate of $\mathrm{Ru(O)(py)(pap)_2^{2+}}$. It reacts rapidly with neutral water to regenerate the parent complex. Further studies on characterization are on.

(34) A similar reaction also takes place in 1 M sulfuric acid medium. However, the process of regeneration is much slower here. Hence for the synthesis of salts of $\mathrm{Ru(O)(py)(pap)_2^{2+}}$, 1 M $\mathrm{H_2SO_4}$ could be a good medium.[33]

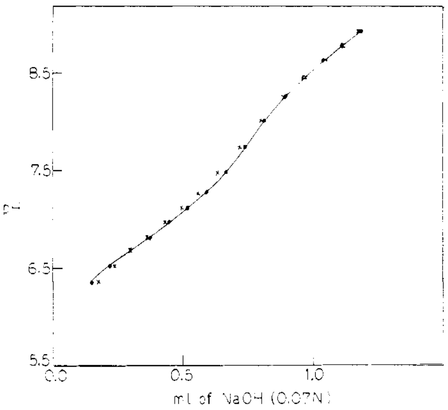

Figure 4. Titration curve of *tc*-$[Ru(OH_2)_2(pap)_2](ClO_4)_2{\cdot}H_2O$ in a 80:20 water–dioxane mixture. The line connecting the solid dots (●) is the experimental curve, and the crosses (×) denote calculated data points.

$(ClO_4)_2{\cdot}H_2O$ (in 80:20 water–dioxane) or *tc*-$[Ru(OH_2)(py)(pap)_2](ClO_4)_2{\cdot}H_2O$ (in water) with use of a Type 335 Systronics pH meter in a double-walled glass vessel thermostated at 298 K. Carbonate-free[35] sodium hydroxide solution (0.073 N) was added from a buret that could be read accurately to 0.01 mL.

In the case of the diaquo complex relation 25 holds.[30,36] Here $[Na^+]$

$$\frac{\bar{h}}{2-\bar{h}}[H^+]^2 = \frac{1-\bar{h}}{2-\bar{h}}[H^+]K_1 + K_1K_2 \tag{25}$$

$$\bar{h} = \frac{[Na^+]}{a} \tag{26}$$

is the concentration of Na^+ coming from added NaOH, a is the total concentration of the complex, and K_1 and K_2 are the equilibrium constants of reactions 12 and 13. Values of $(\bar{h}/(2-\bar{h}))[H^+]^2$ were plotted against those of $((1-\bar{h})/(2-\bar{h}))[H^+]$. An excellent linear plot resulted. The parameters K_1 and K_1K_2 were obtained from the slope and intercept, respectively. A typical titration curve and the calculated curve are displayed in Figure 4.

In case of the monoaquo complex *tc*-$[Ru(OH_2)(py)(pap)_2](ClO_4)_2{\cdot}H_2O$ eq 27 holds,[37] where a is the total concentration of the

$$pK = pH - \log\left(\frac{[Na^+]}{a-[Na^+]}\right) \tag{27}$$

complexes. A solute concentration of at least 5×10^{-3} M was essential for accurate monitoring of pH changes during titration. Attempts to keep the ionic strength constant by adding excess sodium perchlorate, nitrate, or chloride were vitiated by precipitation and/or anation of the complex. The present results therefore do not correspond to constant ionic strength.

In electrochemical and spectrophotometric measurements the pHs of the solutions were adjusted by adding the required amount of aqueous sodium hydroxide or perchloric acid solutions. Immediately before and after each measurement the pH was measured accurately with the help of the pH meter.

Preparation of Complexes. *tc*-Diaquobis[2-(phenylazo)pyridine]ruthenium(II) Perchlorate Hydrate, *tc*-$[Ru(OH_2)_2(pap)_2](ClO_4){\cdot}H_2O$. To a suspension of 0.25 g (0.35 mmol) of *tc*-$RuCl_2(pap)_2$ in 15 mL of water was added 0.20 g (0.96 mmol) of $AgClO_4$. The mixture was then heated to reflux for 2 h. The solution gradually turned red-violet, and precipitation of white AgCl occurred. The reaction mixture was then allowed to cool to room temperature. It was filtered through a sintered-glass funnel (G4). To the filtrate was added a large excess of sodium perchlorate (10 g) and 1 mL of 70% aqueous perchloric acid. Immediately crystals started depositing, which were collected by filtration. The dark-colored crystals were then redissolved in the minimum volume of boiling water, and the solution was filtered in a hot condition. The solution was kept in the refrigerator for 24 h. Needle-shaped dark-colored crystals resulted. These were collected by filtration and dried under vacuum over P_4O_{10}. The yield was 75%.

The tap analogues of the *tc* and *cc* isomers were prepared with use of the same reaction stoichiometry and conditions starting with *tc*-$RuCl_2(tap)_2$ and *cc*-$RuCl_2(tap)_2$, respectively. The yields were 70% and 60%, respectively.

***tc*-Bis(benzonitrile)bis[2-(tolylazo)pyridine]ruthenium(II) Perchlorate Hydrate, *tc*-$[Ru(PhCN)_2(tap)_2](ClO_4)_2{\cdot}H_2O$.** A 0.20-g (0.27-mmol) amount of *tc*-$[Ru(OH_2)_2(tap)_2](ClO_4)_2{\cdot}H_2O$ was added to 15 mL of benzonitrile. The mixture was heated to reflux for 2 h. The initial red-violet solution gradually turned to yellow-orange. The reaction mixture was then cooled to room temperature. It was then poured into 50 mL of diethyl ether. Immediately orange crystals started depositing. These were collected by filtration and were dried under vacuum over P_4O_{10}. The yield was 40%.

***tc*-Hydroxoaquobis[2-(phenylazo)pyridine]ruthenium(II) Perchlorate Hydrate, *tc*-$[Ru(OH)(OH_2)(pap)_2]ClO_4{\cdot}H_2O$.** A 0.25-g (0.35-mmol) amount of *tc*-$[Ru(OH_2)_2(pap)_2](ClO_4)_2{\cdot}H_2O$ was added to 25 mL of water, and the mixture was stirred magnetically at room temperature. Carbonate-free aqueous sodium hydroxide (0.01 N) was added dropwise to the stirred solution until the pH became 8. Then 5 mL of a saturated aqueous solution of sodium perchlorate was added to the reaction mixture. Almost quantitative precipitation occurred. The blue-violet crystalline precipitate was collected and was washed thoroughly with dilute aqueous sodium hydroxide solution (pH ~8). It was then dried under vacuum over P_4O_{10}. The yield was 85%.

***tc*-Dihydroxobis[2-(phenylazo)pyridine]ruthenium(II) Hydrate, *tc*-$Ru(OH)_2(pap)_2{\cdot}H_2O$.** A 0.25-g (0.35-mmol) amount of *tc*-$[Ru(OH_2)_2(pap)_2](ClO_4)_2{\cdot}H_2O$ was added to 20 mL of carbonate-free aqueous (0.1 M) sodium hydroxide under a dinitrogen atmosphere. Immediately the color became inky blue. The solution was concentrated to ~5 mL by evaporation under vacuum. Crystals with a bronze sheen deposited gradually. The mass was then extracted with 15 × 3 mL of dichloromethane. The dichloromethane extract was added to 30 mL of petroleum ether (60–80 °C). The mixture was then allowed to evaporate under a dinitrogen atmosphere at 40 °C. The solution gradually became colorless, and blue crystals deposited. The collected crystals were redissolved in the minimum volume (~20 mL) of dichloromethane, and the crystallization procedure was repeated once more. The crystals thus obtained were dried under vacuum over P_4O_{10}. The yield was 50%.

***tc*-Aquo(pyridine)bis[2-(phenylazo)pyridine]ruthenium(II) Perchlorate Hydrate, *tc*-$[Ru(OH_2)(py)(pap)_2](ClO_4)_2{\cdot}H_2O$. Procedure 1.** A 0.25-g (0.35-mmol) amount of *tc*-$[Ru(OH_2)_2(pap)_2](ClO_4)_2{\cdot}H_2O$ was added to 25 mL of water. To the red-violet reaction mixture was added 0.1 g (1.26 mmol) of pyridine. The solution was then stirred at room temperature for 2 h. Gradually the red-violet solution turned to blue-violet. The mixture was then acidified with aqueous perchloric acid, and a large excess of sodium perchlorate was added. Immediately a red precipitate was deposited. It was collected by filtration and then redissolved in boiling water (30 mL). After filtration in a hot condition the filtrate was kept in the refrigerator for 24 h. The dark-colored shining crystals that deposited were collected by filtration. It was then dried under vacuum over P_4O_{10}. The yield was 70%.

Procedure 2. To a suspension of 0.1 g (0.16 mmol) of *tc*-$[Ru(OH)(OH_2)(pap)_2]ClO_4{\cdot}H_2O$ in 15 mL of water was added 0.013 g (0.16 mmol) of pyridine. The mixture was stirred magnetically at room temperature for 2 h. Gradually the reaction mixture turned blue-violet. Succeeding operations were exactly similar to those in procedure 1. The yield was 65%.

tc-$[Ru(OH_2)(pic)(pap)_2](ClO_4)_2{\cdot}H_2O$ was prepared with use of procedure 1 by mere replacement of pyridine by β-picoline. The yield was 60%.

Conversion of *tc*-$[Ru(OH_2)_2(tap)_2](ClO_4)_2{\cdot}H_2O$ to *tc*-$RuCl_2(tap)_2$. A 0.05-g (0.067-mmol) amount of *tc*-$[Ru(OH_2)_2(tap)_2](ClO_4)_2{\cdot}H_2O$ was dissolved in 15 mL of water. To this was added a 10× excess of LiCl. The solution was stirred magnetically at approximately 40 °C for 1 h. The blue crystals that deposited from the reaction mixture were extracted with $CHCl_3$. Slow evaporation of $CHCl_3$ solution yielded *tc*-$RuCl_2(tap)_2$.

The *cc* diaquo complex was similarly converted to the corresponding *cc* dichloro complex.

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Registry No. *tc*-2 (L = pap), 84027-71-4; *tc*-2 (L = tap), 81600-80-8; *cc*-3 (L = tap), 84049-23-0; *tc*-5 (L = pap), 84027-70-3; *tc*-5 (L = tap), 84027-73-6; *tc*-5 (L = pap), 84027-78-1; *cc*-6 (L = tap), 84049-25-2; *tc*-7 (L = pap), 84027-80-5; *tc*-8 (L = pap), 84027-77-0; $AgClO_4$, 7783-93-9; MeCN, 75-05-8; PhCN, 100-47-0; *tc*-$[Ru(PhCN)_2(tap)_2](ClO_4)_2$, 84027-75-8; *tc*-$[Ru(OH)_2(pic)(pap)_2](ClO_4)_2$, 84027-82-7; py, 110-86-1.

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Stabilities of Mononuclear and Dinuclear Macrocyclic Complexes of 1,4,7,13,16,19-Hexaaza-10,22-dioxacyclotetracosane (bisdien)

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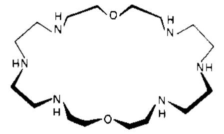
Potentiometric equilibrium studies of the stability constants of the macrocyclic metal complexes of 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane (bisdien) with Cu(II), Co(II), Ni(II), and Zn(II) are reported. Equilibrium data are determined for the formation of mononuclear and dinuclear chelates of these metal ions, as well as several protonated and hydroxo chelates. The ligand is flexible enough to form stable mononuclear macrocyclic complexes in which from four to six of the basic nitrogen donors seem to be coordinated to the metal ion. The dinuclear complexes are less stable than those of the closely related cryptand ligand bistren, but the dinuclear Cu(II) chelate is sufficiently stable to form extensively in solution and is further stabilized by a bridging hydroxide ion in neutral- and high-pH solution. The dinuclear complexes of Co(II) and Cu(II) are stabilized by secondary ligands that provide two- or three-atom bridges between the metal ions. Thus neutral imidazole and the imidazolate anion form stable, cascade type, bridged dinuclear Cu(II) complexes of the macrocycle. Dioxygen forms a stable dibridged (peroxo- and hydroxo-bridged) dicobalt complex. Ethylenediamine and glycine do not appear to be bridging donors for dinuclear bisdien complexes, but ethylenediamine combines with the dicopper(II) complex of the macrocyclic ligand to form relatively weak mixed-ligand complexes.

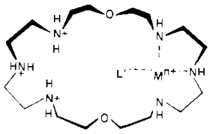
Introduction

Macrocyclic ligands containing two chelating subunits linked by two bridges may form both mononuclear and dinuclear complexes with metal cations. In the latter, the distance and arrangement in space of the two metal centers are determined by the structure of the bridges, whereas their properties depend on the nature of the chelating sites; furthermore, with suitable macrocycles, cascade complexes may form by subsequent uptake of a substrate bridging the two metal ions (for general considerations, see ref 1).

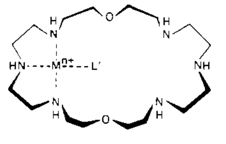
The macrocyclic hexamine bisdien (1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane or [24]ane-N_6O_2 (**1**)) is such a bis chelating macrocycle: it contains two diethylenetriamine units separated by two five-atom bridges. Although the ether oxygens located at the centers of these bridges may have weak coordinating tendencies toward certain metal ions, they may be neglected in considering the complexes that are formed with first-row transition metals described in this report. It is of interest to determine whether this macrocyclic hexamine, **1**, will form stable mononuclear complexes of the type indicated by **2** and **3**. The flexibility of the two five-atom bridges probably would allow the six basic nitrogen atoms in the ligand to coordinate to a single metal ion, although with considerable loss of entropy. Conceivably, dinuclear complexes such as **4** may also form, especially in the presence of additional mono-, di-, or tridentate ligands, resulting in the formation of mixed-ligand dinuclear complexes such as **5** and **6**.



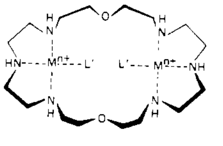
1 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane (BISDIEN, L)



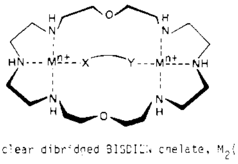
2 Protonated mononuclear BISDIEN chelate, $MH_3L'L^{(3+n)+}$ (L' = solvent molecule)



3 Mononuclear BISDIEN chelate $ML'L^{n+}$ (L' - solvent molecule)



4 Binuclear BISDIEN chelate, $M_2L'_2L^{2n+}$ (L' = solvent molecule)



5 Binuclear dibridged BISDIEN chelate, $M_2(X\text{-}Y)L^{2n+}$ (X-Y = neutral bidentate ligand)

The synthesis of **1** has been performed in the course of the study of the macrobicyclic dinucleating ligand bistren[2] (7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo-[11.11.11]pentatriacontane), and a more direct procedure has been developed more recently.[3] In the presence of azide ions, **1** forms a dinuclear copper(II) cryptate, $[(N_3)_2Cu,Cu(N_3)_2 \subset \mathbf{1}]$, in which the two metal ions are contained inside the macrocyclic ligand; its structure and magnetic properties have been studied.[3] Recent papers have reported the formation of cascade complexes in which the two metal ions of the dinuclear copper(II) complex of **1** are bridged by an imidazolate[4] or hydroxide[5] anion.

In view of these results, it appeared of interest to determine the possible role of bridging ligands in stabilizing and pro-

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