is larger in Mo(O)(MEC) than in Mo(O)(TPP)(X).

The Soret, α, and β bands of Mo(O)(MEC) were observed in regions lower by ca. 20 nm than the corresponding bands of molybdenum porphyrins. This seems to be consistent with the above discussion. The Soret, α, and β bands of the molybdenum porphyrin complexes depend on the nature of the axial ligand trans to the oxo group and are shifted to longer wavelength in the order MeO < AcO < Cl. Similar results have been obtained for the octaethylporphyrin complexes.[21] The value of $\Delta E_{1/2}{}^{\mathrm{Ox/Red}}$ is independent of the nature of axial ligands, 0.35–0.40 V. This would indicate that the Soret, α, and β bands are not referred to exclusive π–π^* transitions within ligand molecules but to intramolecular charge-transfer transitions such as a $a_{2u}a_{1u}(\pi) \rightarrow e_g(d\pi)$, at least in part. The energy levels of molybdenum d orbitals seem to be subjected to change by effective electronegativity of the metal. Less intense bands that appeared in the 500–600-nm region also reduced their intensities as the number of d electrons decreased from two to zero in regards to Mo(O)(MEC). The result further indicates that the less intense bands are primarily due to metal(d) → ligand(π^*) charge-transfer transitions. Although Mo(O)(MEC) and **1** have almost identical reduction potentials for the central molybdenum, the difference of their oxidation potentials is more than 1.0 V. Corrole serves as a trinegative ligand, so that Mo(V) ion binds the tetrapyrrolic ligand to form a square-pyramidal coordination structure with an oxo group at the top, the complex being electrically neutral. Since porphyrin is a dinegative ligand, the molybdenum(V) complex having an oxo group needs to take up another monoanionic ligand in order to satisfy electric neutrality. As mentioned above, the Mo–Cl bond in **3** has an appreciable ionic character; a positive charge localized at the molybdenum atom may facilitate the metal reduction. On the other hand, the Mo–OMe bond has a considerable covalent character, and, consequently, such a positive charge must be efficiently delocalized. This view is consistent with the fact that the molybdenum atom of **1** has a reduction potential identical with that of Mo(O)(MEC). Facile oxidation of the central molybdenum in Mo(O)(MEC) compared with **1** can be explained in terms of delocalization of the positive charge (formally on Mo) throughout the π-electron system involving the oxo group and the macrocyclic ligand via d_{xz} and d_{yz} orbitals since the Mo=O stretching vibration is greater for Mo(O)(MEC) than for **1**. In any case, the oxidation of molybdenum is more facile for $\mathrm{Mo^{V}(O)(MEC)}$ than for $\mathrm{Mo^{V}}$–porphyrins due to the difference in charge density at the molybdenum atom as reflected on A_{Mo} values (Table I).

$\mathrm{Mo^{V}(O)(MEC)}$ has no coordination tendency at the axial site trans to the oxo group. The electronic absorption spectra of this complex measured in pyridine, tetrahydrofuran, dichloromethane, and dichloromethane–methanol were almost identical, and also the ESR spectrum in pyridine was identical with that measured in dichloromethane. These results suggest that the Mo=O bond is sufficiently strong, and the complex has a square-pyramidal structure with a molybdenum atom displaced from the ligand plane, so that the sixth coordination site has no practical coordination ability. Even though Mo(O)(TPP) takes up a monoanionic ligand at the site trans to the oxo group, this site is quite labile for substitution reaction. The molybdenum(V) ion has a strong affinity for oxygen, its hard acid character being reflected. Thus, an equilibrium for the reaction between **1** and chloride ion, a hard base, was achieved instantaneously, but the reaction of **1** with a more soft base, bromide ion, was too slow to obtain equilibrium constant.

Acknowledgment. We wish to thank Mr. H. Horiuchi, glassworker of our department, for his skill in preparing three-electrode cells used for controlled-potential electrolysis. This work was supported in part by the Asahi Glass Foundation for Industrial Technology.

Registry No. **1**, 74751-79-4; **2**, 77320-98-0; **3**, 77320-99-1; Mo(O)MEC, 63621-40-9; Mo(O)TPP(ClO_4), 77321-00-7; $[\mathrm{Mo(O)(MEC)}]^-$, 74751-80-7; $[\mathrm{Mo(O)(MEC)}]^+$, 74751-81-8; $\mathrm{Mo^{IV}(O)TPP}$, 33519-60-7; H_3MEC, 73227-36-8; H_2TPP, 917-23-7.

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[21] Gouterman, M. *Porphyrins* **1977**, *3*, Chapter 1.

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Chemistry of Ruthenium. 2.[1] Synthesis, Structure, and Redox Properties of 2-(Arylazo)pyridine Complexes

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Two types of ruthenium(II) complexes RuX_2L_2 (green) and $[Ru(bpy)_2L](ClO_4)_2{\cdot}H_2O$ (red) are reported (X = Cl, Br, I; L = 2-(phenylazo)pyridine or 2-(*m*-tolylazo)pyridine; bpy = 2,2′-bipyridine). The RuX_2L_2 species systematically displays single RuX and RuN(pyridine) stretches in the far IR, strongly suggesting a centrosymmetric configuration for the coordination sphere. Both types of complexes have intense $t_2(\mathrm{Ru}) \rightarrow \pi^*(\mathrm{L})$ transitions in the visible region. $RuCl_2L_2$ is unreactive to Ag^+ and nitrogen bases; monodentate tertiary phosphines (P) however give $RuClPL_2{}^+$. Both RuX_2L_2 and $Ru(bpy)_2L^{2+}$ exhibit reversible or nearly reversible ruthenium(III)–ruthenium(II) couples at platinum electrode. The $E°_{298}{}'$ values in acetonitrile are ~+0.9 V for $RuX_2L_2{}^+/RuX_2L_2$ and ~+1.60 V for $Ru(bpy)_2L^{3+}/Ru(bpy)_2L^{2+}$ vs. SCE. The azopyridine ligand system greatly stabilizes the +2 oxidation state in ruthenium. The complexes also display electrochemical responses on the negative side of SCE due to ligand-based reductions. Azo reduction occurs quasi-reversibly at ~−0.5 V in $Ru(bpy)_2L^{2+}$. The existence of a blue isomer of RuX_2L_2 (X = Cl, Br) having *cis*-RuX_2 is briefly noted.

Introduction

The ruthenium chemistry of chelating aromatic nitrogenous ligands has primarily grown around[2–7] pyridine bases, particularly 2,2′-bipyridine (bpy), and related species. In the course of a systematic search[1] for new ruthenium complexes,

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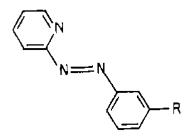
[1] Part 1: Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 275. See also: Chakravarty, A. R.; Chakravorty, A. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 307.

[2] Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 3374. Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1064.

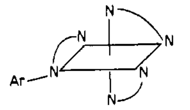
[3] Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660.

we have discovered several groups of chelates based on azopyridine ligand systems which have the N=CN=N chromophore. The synthesis, characterization, and electron-transfer behavior of two such groups, viz., RuX_2L_2 (X = Cl, Br, I) and $Ru(bpy)_2L^{2+}$ derived from 2-(phenylazo)pyridine (pap) and 2-(*m*-tolylazo)pyridine (tap), are reported in this work (general abbreviations for the two ligands (**1**) is L).



pap, R=H
tap, R=Me

1



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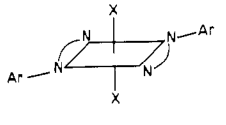

3

Experimental Section

Materials. 2-(Phenylazo)pyridine was synthesized by condensing 2-aminopyridine with nitrosobenzene according to reported procedure[8] with the modification that chromatographic purification was done on a column of silica gel instead of alumina. On silica gel a better separation of bands was achieved. 2-(*m*-Tolylazo)pyridine was similarly prepared by simply replacing nitrosobenzene by *m*-nitrosotoluene in the above procedure. Ruthenium trichloride, $RuCl_3{\cdot}3H_2O$, was purified as before.[1] *cis*-$RuCl_2(bpy)_2{\cdot}2H_2O$ was prepared by using a published procedure.[9] Acetonitrile for electrochemical studies was prepared by CaH_2 and P_4O_{10} treatment of the commercial solvents. Electrochemically pure dichloromethane was prepared from the commercial solvent by treatment of $NaHCO_3$ and anhydrous $CaCl_2$. Tetraethylammonium perchlorate (TEAP) was prepared as before.[1]

Measurements. Electronic spectra were recorded with a Cary 17D spectrophotometer; IR spectra (KBr disk, 4000–400 cm^{-1}; polyethylene disk, 400–100 cm^{-1}) were obtained with Beckman IR-20A and IR-720M spectrophotometers. ^1H NMR data were collected in $CDCl_3$ solvent with a Varian T-60 spectrometer. Solution electrical conductivity was measured with use of a Philips PR9500 bridge with a solute concentration of $\sim 10^{-3}$ M. Electrochemical measurements (cyclic voltammetry, phase-sensitive ac voltammetry, controlled-potential coulometry) were carried out with the help of a PAR 174A polarographic analyzer, PAR 175 universal programmer, PAR 124A lock-in amplifier, PAR 372 ac polarography interface, PAR RE0074 X-Y recorder, PAR 173 potentiostat, PAR 179 digital coulomter, and PAR 377A cell system. The three electrode measurements were carried out with use of a planar Beckman Model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE). For coulometry a platinum-wire-gauge working electrode was used. Coulometric data are averages of at least three independent measurements. The results were collected at 298 ± 1 K and are uncorrected for junction potentials.

Preparation of Complexes. Dichlorobis(2-(phenylazo)pyridine)ruthenium(II), $RuCl_2(pap)_2$. Nitrogen gas was passed for 15 min through a brown solution of 0.13 g (0.5 mmol) of $RuCl_3{\cdot}3H_2O$ in 15 mL of methanol. Then 0.2 g (1.09 mmol) of pap in 5 mL of methanol was added. The green mixture was heated to reflux under a nitrogen atmosphere with magnetic stirring for 8 h. During this period the solution turned blue and a green precipitate deposited. After the solution was cooled to room temperature, the precipitate was collected by filtration and washed thoroughly with water and finally with diethyl ether. It was then dried in a vacuum desiccator over P_4O_{10}. The dried product was dissolved in a small volume of $CHCl_3$ and was subjected to chromatography on a silica gel (60–120 mesh) column (30 × 1 cm). A green band was eluted with CH_2Cl_2. A blue band remained near the top of the column. Crystals were obtained by complete evaportion of the deep green CH_2Cl_2 eluate at room temperature. The yield was 0.19 g (69%). Anal. Calcd for $RuC_{22}H_{18}N_6Cl_2$: C, 49.06; H, 3.34; N, 15.61; Cl, 13.19. Found: C, 49.49; H, 3,83; N, 15.15; Cl, 13.30. The *bromo analogue*, $RuBr_2(pap)_2$, was prepared by using the same reactant stoichiometry and procedure except that 3 g of LiBr was added to the methanolic solution of $RuCl_3{\cdot}3H_2O$ prior to the addition of the ligand. The yield was 0.18 g (57%). Anal. Calcd for $RuC_{22}H_{18}N_6Br_2$: C, 42.09; H, 2.87; N, 13.39. Found: C, 42.60; H, 3.20 N, 13.08.

Dichlorobis(2-(*m*-tolylazo)pyridine)ruthenium(II), $RuCl_2(tap)_2$. This was prepared similarly. Only pap was replaced by an equivalent amount of tap. The yield was 0.18 g (61%). Anal. Calcd for $RuC_{24}H_{22}N_6Cl_2$: C, 50.87; H, 3.88; N, 14.84; Cl, 12.54. Found: C, 51.23; H, 4.17; N, 14.48; Cl, 12.60. The *bromo analogue*, $RuBr_2(tap)_2$, was prepared using the same stoichiometry and procedure except that 3 g of LiBr was added to the methanolic solution of $RuCl_3{\cdot}3H_2O$ prior to the addition of the ligand. The yield was 0.18 g (55%). Anal. Calcd for $RuC_{24}H_{22}N_6Br_2$: C, 43.96; H, 3.36; N, 12.81. Found: C, 44.41; H, 3.63; N, 12.50.

Diiodobis(2-(phenylazo)pyridine)ruthenium(II), $RuI_2(pap)_2$. To a nitrogen flushed solution of 0.13 g (0.5 mmol) of $RuCl_3{\cdot}3H_2O$ in 15 mL of methanol was added 4.5 g of NaI. After the mixture was magnetically stirred for 45 min at room temperature, 0.2 g (1.09 mmol) of pap in 5 mL of methanol was added. Stirring *at room temperature* was continued for 8 h. Gradually the solution turned green, and a green precipitate was formed. This was collected, washed, dried, and finally put on a silica gel column as in the case of $RuCl_2L_2$. A green band was then eluted with benzene (in this case no slow-moving blue band was observed). Evaporation of solvent from the benzene eluate gave crystals of the complex. The yield was 0.23 g (64%). Anal. Calcd for $RuC_{22}H_{18}N_6I_2$: C, 36.61; H, 2.49; N, 11.64. Found: C, 36.80; H, 2.80; N, 11.29. The *tap analogue* was prepared similarly. Only pap was replaced by an equivalent amount of tap. The yield was 0.2 g (53%). Anal. Calcd for $RuC_{24}H_{22}N_6I_2$: C, 38.44; H, 2.94; N, 11.21. Found: C, 38.80; H, 3.11; N, 11.01.

All RuX_2L_2 complexes form shining green crystals with a bronze sheen. They are soluble in $CHCl_3$, CH_2Cl_2, and CH_3CN, sparingly soluble in C_6H_6 and CH_3OH, and insoluble in H_2O. All solutions are green and are nonconductors of electricity.

Bis(bipyridine)(2-(phenylazo)pyridine)ruthenium(II) Perchlorate Monohydrate, $[Ru(bpy)_2(pap)](ClO_4)_2{\cdot}H_2O$. To a suspension of 0.1 g (0.18 mmol) of *cis*-$RuCl_2(bpy)_2$ in a 1:1 methanol–water mixture was added 0.05 g (0.27 mmol) of pap. The mixture was heated to reflux under nitrogen atmosphere for 3.5 h. The initial violet solution gradually turned red. After being cooled to room temperature, the reaction mixture was filtered, and 5 mL of a saturated aqueous solution of $NaClO_4$ was added to the filtrate. Crystals started depositing immediately. After the mixture was kept in the refrigerator for 24 h, the crystals were filtered, washed thoroughly with cold water, and dried under vacuum over P_4O_{10}. The yield was 0.07 g (50%). Anal. Calcd for $RuC_{31}H_{27}N_7Cl_2O_9$: C, 45.75; H, 3.32; N, 12.05. Found: C, 45.70; H, 3.25; N, 12.00. The *tap analogue* was prepared similarly. Only pap was replaced by an equivalent amount of tap. The yield was 0.08 g (50%). Anal. Calcd for $RuC_{32}H_{29}N_7Cl_2O_9$: C, 46.42; H, 3.50; N, 11.85. Found: C, 46.40; H, 3.44; N, 11.85.

Both complexes occur as shining red crystals which are highly soluble in CH_3OH and CH_3CN, soluble in H_2O, sparingly soluble in $CHCl_3$, and insoluble in C_6H_6.

Results and Discussion

Some iron(II) and nickel(II) complexes of pap were reported earlier.[10] The six RuX_2L_2 complexes reported here all are diamagnetic, stable in air, and nonelectrolytic in organic solvents. In the synthetic reaction involving RuX_3 and L in

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(4) Johnson, E. C.; Callahan, R. W.; Eckberg, R. P.; Hatfield, W. E.; Meyer, T. J. *Inorg. Chem.* **1979**, *18*, 618.

(5) Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298.

(6) Sagüge's, J. A. A.; Gillard, R. D.; Lancashire, R. J.; Williams, P. A. *J. Chem. Soc., Dalton Trans.* **1979**, 193.

(7) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310.

(8) Campbell, N.; Henderson, A. W.; Taylor, D. *J. Chem. Soc.* **1953**, 1281.

(9) Giordano, P. J.; Bock, C. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 6960.

(10) Raghavendra, B. S.; Chakravorty, A. *Indian J. Chem., Sect. A* **1976**, *14A*, 166.

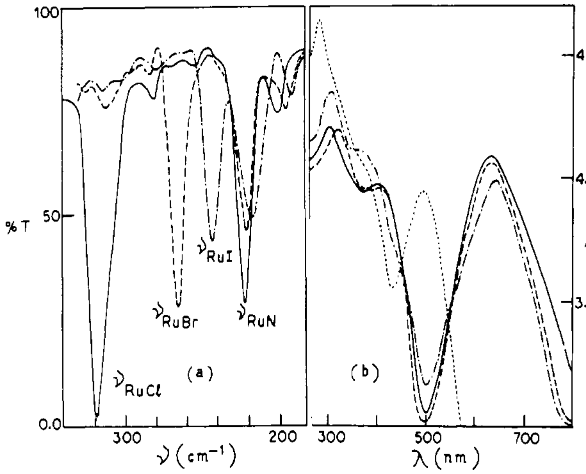

Figure 1. (a) Far-IR spectra of $RuX_2(pap)_2$ in polyethylene disk: —, X = Cl; ---, X = Br; –·–, X = I. (b) Visible–UV spectra of $RuX_2(pap)_2$ in dichloromethane: —, X = Cl; ---, X = Br; –·–, X = I. Visible–UV spectra of $[Ru(bpy)_2(pap)](ClO_4)_2 \cdot H_2O$ in acetonitrile: ····.

methanol solvent, the stage at which the reduction of ruthenium(III) occurs has not been established; electrochemical studies (vide infra) show $RuX_2L_2^+$ species to be strong oxidants. The two diamagnetic $[Ru(bpy)_2L](ClO_4)_2 \cdot H_2O$ complexes obtained by nucleophilic displacement of chloride from *cis*-$RuCl_2(bpy)_2$ by L are 1:2 electrolytic in acetonitrile (for L = pap, $\Lambda = 233\ \Omega^{-1}\ cm^2\ mol^{-1}$; for L = tap, $\Lambda = 246\ \Omega^{-1}\ cm^2\ mol^{-1}$). All the RuX_2L_2 chelates ($[Ru(bpy)_2L](ClO_4)_2 \cdot H_2O$ is insufficiently soluble in $CDCl_3$ for ^1H NMR work) give rise to sharp ^1H NMR signals; the position of the singlet methyl signal of $RuX_2(tap)_2$ is virtually independent of X (δ_{Me} 2.20 in $CDCl_3$). We wish to note that reported ruthenium chelates of azo ligands are sparse.[11]

Infrared Spectra and Structure. The mixed tris bidentate cation, $Ru(bpy)_2L^{2+}$ can have only one chiral structure, viz., **2**. On the other hand, because of the unsymmetrical bidentate nature of L, five geometrically isomeric structures are possible for RuX_2L_2: three isomers with *cis*-RuX_2 orientation and two isomers with *trans*-RuX_2 orientation. The cis isomers are chiral; the trans species are expected to be optically inactive unless unusual distortions make them chiral. In general the isolated green RuX_2L_2 complexes display an intense, sharp, and *single* stretching frequency in the range 350–250 cm^{-1} assignable to ν_{RuX} and a band in the region 225–210 cm^{-1} due[12] to $\nu_{RuN(pyridine)}$. The RuX stretch shifts systematically to lower energies in moving from Cl to Br to I (Figure 1, Table I). Presence of *trans*-RuX_2 grouping is indicated. The associated RuL_2 coordination plane is believed to have the trans configuration (**3**) which is expected to display[12] only one RuN(pyridine) stretch as is actually observed. The cis configuration (two RuN(pyridine) stretches expected here) is unlikely to be obtainable due to steric proximity of the two aryl (Ar) rings. The steric control of isomer preference is of general applicability for planar M(bidentate)$_2$ species.[13] All the complexes display many characteristic infrared group frequencies (e.g., $\nu_{C=N} = 1600\ cm^{-1}$ and $\nu_{N=N} = 1450–1465\ cm^{-1}$) for L as in the case[10] of iron(II) and nickel(II) chelates of pap. These are not considered any further. $[Ru(bpy)_2L](ClO_4)_2 \cdot H_2O$ shows bands at 1100 and 620 cm^{-1} due to ClO_4^- and at 3400 cm^{-1} due to H_2O.

Table I. Selected Infrared and Visible–Ultraviolet Spectral Data

compd	IR[a,b] ν_{max}, cm^{-1} RuX	RuN(pyridine)	vis-UV[e] λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)
$RuCl_2(pap)_2$	319	222	635 (12 150), 402 (9550), 302 (16 250)
$RuBr_2(pap)_2$	265	220	635 (11 550), 402 (9000), 320 (15 550)
$RuI_2(pap)_2$	244	219	642 (10 100), 404 (9700),[f] 360 (12 750), 306 (22 650)
$RuCl_2(tap)_2$	328,[c] 311[c]	215	634 (11 550), 416 (10 050), 302 (16 550)
$RuBr_2(tap)_2$	265	214	635 (11 100), 416 (9550), 318 (15 500)
$RuI_2(tap)_2$	243	211	641 (9800), 402 (11 600),[f] 358 (13 900), 308 (24 550)
$[Ru(bpy)_2(pap)](ClO_4)_2 \cdot H_2O$		*d*	494 (8880), 364 (12 270),[f] 278 (45 000)
$[Ru(bpy)_2(tap)](ClO_4)_2 \cdot H_2O$		*d*	494 (8550), 368 (11 600),[f] 280 (44 500)

[a] In polyethylene disk (400–100 cm^{-1}). [b] All bands are sharp and strong. [c] Origin of the doublet structure is not clear. [d] Measurements were not made. [e] RuX_2L_2 in dichloromethane and $[Ru(bpy)_2L](ClO_4)_2 \cdot H_2O$ in acetonitrile. [f] Shoulder.

Electronic Spectra. Major absorption bands of the complexes appearing above 300 nm are shown in Figure 1 and Table I. Free 2-arylazopyridine ligands display absorption bands at ~440 nm ($\epsilon \approx 700$) and at ~320 nm ($\epsilon \approx 19000$). These can be respectively assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions centered primarily on the azo group.[14] In RuX_2L_2 the latter transition undergoes a slight blue shift (in the order Cl > Br > I) and the former is replaced by an intense absorption at ~400 nm. More significantly an allowed band appears near 640 nm. This band is assigned to a $t_2(Ru) \rightarrow \pi^*(L)$ transition (MLCT) as in[15,16] Ru-bpy species. In *cis*-$RuX_2(bpy)_2$ the $t_2 \rightarrow \pi^*$ transition lies[15] near 550 nm ($\epsilon \approx 9000$) and its energy is insensitive to the nature of X as is also the case for RuX_2L_2. The origin of the band near 400-nm is less certain; its possible assignment to a second[15] $t_2 \rightarrow \pi^*$ transition is vitiated by the observation that it is also present in the oxidized complex $RuX_2L_2^+$ (vide infra). The spectrum of $Ru(bpy)_2L^{2+}$ is qualitatively similar to that[15] of $Ru(bpy)_3^{2+}$. The energy of the first MLCT band increases in the order $RuX_2L_2 < RuX_2(bpy)_2 < Ru(bpy)_2L^{2+} < Ru(bpy)_3^{2+}$.

Chemical Reactivity. When compared to that in *cis*-$RuCl_2(bpy)_2$, the Ru–Cl bond in $RuCl_2L_2$ shows unusual stability toward both electrophilic and nucleophilic attack. In acetone solution it is totally unreactive toward $AgClO_4$—a reagent which readily converts[17] the bpy complex to $RuCl(bpy)_2(CH_3COCH_3)^+$. In boiling methanol–water mixture $RuCl_2L_2$ fails to react with pyridine bases which are known[15,18] to bring about facile halide displacement in *cis*-$RuCl_2(bpy)_2$ under similar conditions. In the same solvent monodentate tertiary phosphines (P) do displace one (but *not* both) of the halogen atoms, producing red-violet $RuCl(P)L_2^+$ which can be isolated as the perchlorate. In the bpy complex both halogen atoms can be displaced[17] by P. Hydroxide ions convert green $RuCl_2L_2$ to a blue substance in methanol–water mixture probably due to nucleophilic attack[6] in the pyridine ring.

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(11) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2820.
(12) Williams, C. S.; Clark, J. H. *Inorg. Chem.* **1965**, *4*, 350. Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; p 211.
(13) Holm, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241.
(14) Kalia, K. C.; Chakravorty, A. *J. Org. Chem.* **1970**, *35*, 2231.
(15) Bryant, G. M.; Fergusson, J. E.; Powell, H. K. J. *Aust. J. Chem.* **1971**, *24*, 257.
(16) Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4096.
(17) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
(18) Dwyer, F. P.; Goodwin, H. A.; Gyarfar, E. C. *Aust. J. Chem.* **1963**, *16*, 544.

Table II. Cyclic Voltammetric Data[a-c] at the Platinum Electrode (298 K)

	$E°_{298}'$ (ΔE_p)	
compd	Ru(III)-Ru(II)	ligand redn[d]
$RuCl_2(pap)_2$[e]	0.925 (60) 0.965 (270)[f]	
$RuBr_2(pap)_2$	0.950 (60) 0.985 (240)[f]	
$RuI_2(pap)_2$	0.853 (75) 0.910 (220)[f]	
$RuCl_2(tap)_2$	0.907 (65)	−0.730,[g] −0.940[g]
$RuBr_2(tap)_2$	0.897 (65)	−0.720,[g] −0.890[g]
$RuI_2(tap)_2$	0.907 (65)	−0.730,[g] −0.860[g]
$[Ru(bpy)_2(pap)](ClO_4)_2 \cdot H_2O$	1.603 (75)	−0.520 (80), −1.258 (80)
$[Ru(bpy)_2(tap)](ClO_4)_2 \cdot H_2O$	1.600 (80)	−0.525 (75), −1.260 (80)

[a] Meaning and units of symbols are the same as in text. [b] Unless otherwise stated the solvent is acetonitrile. [c] Supporting electrolyte TEAP (0.1 M), solute concentration ~10^{-3} M, scan rate 50 mV s^{-1}. [d] Measurement among RuX_2L_2 species was limited to the tap complex. [e] 8.87 mg of complex exhaustively oxidized at +1.2 V. *Q*: calcd, 1.59 C; found, 1.52 C. [f] In dichloromethane. [g] Cathodic peak potential (see text).

Further details of these and other reactions are being investigated and will be reported in due course.

Redox Activity. The complexes are electroactive at the platinum working electrode and display one redox process on the positive side of the SCE and more than one such process on the negative side. These are studied with use of electrochemical techniques (Table II). All potentials are referenced to SCE.

(a) Ruthenium(III)-Ruthenium(II) Couple. The response in RuX_2L_2 near +0.9 V (Figure 2) is considered first. At slow scan rates (v < 50 mV s^{-1}) in acetonitrile the cyclic voltammetric peak-to-peak separation (ΔE_p) is ~60 mV. In stirred solution electrolysis freely occurred when the potential is kept fixed on the positive side of the anodic peak but at potentials less than the cathodic peak little electrolysis is observable. Exhaustive electrolysis (coulometry) of $RuCl_2(pap)_2$ at +1.2 V gives a coulomb count corresponding to the transfer of 1 e/ruthenium atom. The cyclic voltammetric response is thus due to the reversible couple (eq 1), in which $RuX_2L_2^+$ has

$$RuX_2L_2^+ + e^- \rightleftharpoons RuX_2L_2 \qquad (1)$$

ruthenium in the formal oxidation state +3. The formal electrode potentials $E°_{298}'$ (i.e., the average of anodic and cathodic peak potentials) for the couple (eq 1) are collected in Table II. With an increase in the scan rate ($v \geq 100$ mV s^{-1}) and particularly with a change in the solvent to dichloromethane, significant deviation (ΔE_p > 60 mV) from reversibility is noticed (Table II). Electron-transfer rate is slower in dichloromethane than in acetonitrile.

For every RuX_2L_2 complex the process in eq 1 was also studied in acetonitrile solution by using phase-sensitive alternating-current cyclic voltammetry[19] (Figure 2). The peak potentials for forward (anodic) and backward scans nearly coincided with each other at low dc scan rates, thus confirming the reversibility of the process (cf. cyclic voltammetry). The peak potential or more accurately the crossover potential[19] for forward and backward scans agreed well (within ±10 mV) with the cyclic voltammetric $E°_{298}'$. At sinusoidal frequencies of 20-40 Hz the width at half-height was found to lie in the range 100-120 mV, showing that the electrode process is approximately ac reversible.[19]

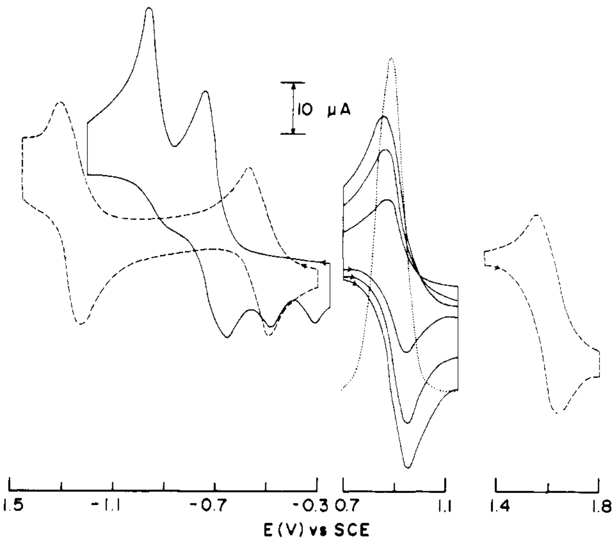

Figure 2. Segmented voltammograms in acetonitrile (0.1 M TEAP) at platinum electrode (298 K). Region 1.8-1.4 V: ---, dc cyclic of $[Ru(bpy)_2(tap)](ClO_4)_2 \cdot H_2O$ at a scan rate of 50 mV s^{-1}. Region 1.1-0.7 V: —, dc cyclic of $RuCl_2(tap)_2$ at three different scan rates (100, 300, and 500 mV s^{-1}); ···, phase-sensitive ac cyclic of $RuCl_2(tap)_2$ at a sinusoidal frequency of 22 Hz and a dc scan rate of 0.5 mV s^{-1}. Region −0.3 to −1.5 V: —, dc cyclic of $RuCl_2(tap)_2$ at a scan rate of 50 mV s^{-1}; ---, dc cyclic of $[Ru(bpy)_2(tap)](ClO_4)_2 \cdot H_2O$ at a scan rate of 50 mV s^{-1}.

The two $Ru(bpy)_2L^{2+}$ species show the ruthenium(III)-ruthenium(II) couple (eq 2) at ~+1.60 V. The couple (eq 2) is quasi-reversible (Table II).

$$Ru(bpy)_2L^{3+} + e^- \rightleftharpoons Ru(bpy)_2L^{2+} \qquad (2)$$

The ruthenium(III)-ruthenium(II) redox potentials of RuX_2L_2 are considerably higher than that of *cis*-$RuCl_2(bpy)_2$ (+0.30 V in dichloromethane)[20] and *trans*-$RuCl_2(HB)(B)^-$ (+0.46 V in acetonitrile (HB = α-benzil monoxime))[1] and several other dichlororuthenium(II) species.[1] The $E°_{298}'$ of $Ru(bpy)_2L^{2+}$ substantially exceeds that of $Ru(bpy)_3^{2+}$ (+1.29 V in dichloromethane).[20] The azopyridine ligand thus stabilizes (in the respect of oxidation) ruthenium(II) better than bpy. Few ruthenium(III)-ruthenium(II) couples are known whose redox potentials exceed that of $Ru(bpy)_2L^{2+}$.

(b) Ligand Reduction. RuX_2L_2 displays two distinct reduction peaks in the range −0.7 to −1.5 V. The reduced species does not appear to be stable and on scan reversal multiple anodic responses of unclear origin are observed (Figure 2). It is believed that the reduction peaks correspond to the reduction of the organic ligand possibility at the azo function. This conjecture is based on available literature[21] and on our own systematic studies[22] on the electrochemical reduction of platinum metal complexes of azo ligands. In the case of $Ru(bpy)_2L^{2+}$ complexes the redox cycles are more well behaved: two quasi-reversible one-electron couples with an $E°_{298}'$ of −0.52 and −1.26 V being observed (Figure 2). The former is believed[22] to be due to the reduction of the azo function of L while the latter reduction may be localized on the bpy ligand.[23]

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(19) Underkolfer, W. L.; Shain, I. *Anal. Chem.* **1965**, *37*, 218. Bond, A. M.; O'Halloran, R. J.; Ruzic, I.; Smith, D. E. *Anal. Chem.* **1976**, *48*, 872.

(20) Johnson, E. C.; Sullivan, B. P.; Salmon, D. J.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 2211.

(21) Sadler, J. L.; Bard, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 1979. Darbrowiak, J. C.; Fisher, D. P.; McElroy, F. C.; Macero, D. J. *Inorg. Chem.* **1979**, *18*, 2304.

(22) Bandyopadhyay, P.; Mukherjee, R. N.; Ghosh, P.; Chakravorty, A., unpublished results.

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

Concluding Remarks

It is demonstrated that 2-(arylazo)pyridine ligands bind ruthenium(II) remarkably well. Two related groups of complexes of the *trans*-RuX_2 moiety are thoroughly characterized with use of spectroscopic and electrochemical methods. We wish to note that outside halocarbonyl chemistry[24] iodo complexes of ruthenium are limited in number,[15,18,25] and therefore well-characterized triads (X = Cl, Br, I) of dihaloruthenium complexes are relatively uncommon. Reports on the systematic identification of ν_{RuX} as X is varied are lacking.

The oxidation of the present complexes occur at high positive potentials, making the ruthenium(III) species strong oxidants and therefore quite reactive. In the synthesis of RuX_2L_2 from RuX_3 and L, it is quite likely that one or more unstable ruthenium(III) complexes are first formed which then undergo reduction (solvent oxidation?) to yield the final product. Snuff colored $RuCl_2L_2^+$ present in the coulometrically oxidized acetonitrile solution of $RuCl_2L_2$ is not particularly stable and is transformed to green (within 0.5 h) and then to blue (in 24 h) species which have not been fully characterized. A fresh solution of $RuCl_2L_2^+$ shows allowed electronic bands at ~550 and ~400 nm. The former may be of LMCT origin.[26] Attempts to isolate $RuX_2L_2^+$ as salts are under way.

The slow moving blue band remaining (see Experimental Section) on the silica gel column during chromatographic purification of green RuX_2L_2 (X = Cl, Br) yields small amounts of a crystalline blue complex after elution with acetonitrile–benzene mixture. Interestingly, the composition of this complex also corresponds exactly to RuX_2L_2. Evidently RuX_2L_2 (X = Cl, Br) exist as green and blue isomers. Preliminary IR and ^1H NMR data suggest that the blue complex has *cis*-RuX_2 and that it itself may actually be a mixture of more than one isomer differing in RuL_2 stereochemistry. Further studies are currently under way.

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Registry No. $RuCl_2(pap)_2$, 77321-07-4; $RuBr_2(pap)_2$, 77321-08-5; $RuI_2(pap)_2$, 77341-75-4; $RuCl_2(tap)_2$, 77321-09-6; $RuBr_2(tap)_2$, 77321-10-9; $RuI_2(tap)_2$, 77321-11-0; $[Ru(bpy)_2(pap)](ClO_4)_2$, 77321-13-2; $[Ru(bpy)_2(tap)](ClO_4)_2$, 77321-15-4; *cis*-$RuCl_2(bpy)_2$, 19542-80-4.

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[24] Vancea, L.; Graham, W. A. G. *J. Organomet. Chem.* **1977**, *134*, 219. Barnard, C. F. J.; Daniels, J. A.; Jeffery, J.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1861.

[25] Richardson, D. E.; Taube, H. *Inorg. Chem.* **1979**, *18*, 549. Poddar, R. K.; Agarwala, U.; Monoharan, P. T. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2275.

[26] Bryant, G. M.; Fergusson, J. E. *Aust. J. Chem.* **1971**, *24*, 275.

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Electrochemistry of the Intensely Green Complexes Formed by the Reaction of Cr^{2+} with Pyrazine ("Pyrazine Green"), Pyrazinecarboxamide, and Pyrazinecarboxylic Acid

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The electrochemical responses of "pyrazine green" and the "greens" formed by reaction of Cr^{2+} with pyrazinecarboxamide and pyrazinecarboxylic acid are described. Solutions of pyrazine green exhibit a single, composite polarographic wave which passes without inflection from anodic to cathodic currents. The anodic branch corresponds to the oxidation of the green by one electron to produce the pentaaquapyrazine complex of Cr(III). The cathodic branch corresponds to the reduction of the green by two electrons to produce Cr^{2+} and dihydropyrazinium ion. By contrast, the corresponding set of reactions for pyrazinecarboxylic acid green gives rise to separate oxidation and reduction waves. The more complex behavior of the green formed by pyrazinecarboxamide involves two isomers that can be interconverted by a reaction catalyzed by Cr^{2+}. The two isomers have very different electrochemical properties. One of the isomers of pyrazinecarboxamide green and the green formed from pyrazine carboxylic acid are believed to be chelates in which the organic reagent behaves as a bidentate ligand.

The rapid reaction of Cr^{2+} with pyrazines to form the intensely colored "pyrazine greens" has been observed repeatedly.[1-3] The product of the reaction seems best regarded as a complex of Cr(III) with a radical ligand.[3,4] As part of our continuing interest in the role of bridging ligands in catalyzing the oxidation of Cr^{2+} at mercury electrodes,[5] we have carried out electrochemical studies of three "pyrazine greens" and the corresponding products of their oxidation or reduction at electrodes. No previous reports of the electrochemical behavior of these interesting complexes are available.

Experimental Section

Materials. Pyrazine, pyrazinecarboxylic acid, and pyrazinecarboxamide were commercially available reagents (Aldrich Chemical Co.) and were used as received. Chromium(III) perchlorate (G. F. Smith Chem. Co.) solutions were prepared in perchloric acid and were analyzed spectrophotometrically after oxidizing the Cr(III) to CrO_4^{2-}. Mercury(II) perchlorate solutions were prepared by dissolving mercuric oxide in perchloric acid. Sodium perchlorate solutions were prepared by neutralizing perchloric acid with sodium carbonate. Laboratory distilled water was further purified by passage through a Barnstead D2790 Nanopure purification train. Triply distilled mercury (Bethlemen Inst. Co.) was employed. Cation-exchange resins were Dowex 50W-X8 and Sephadex SPC 100-20.

Apparatus and Procedures. Conventional two-compartment electrochemical cells were employed for polarographic voltammetric measurements except when the PAR Model 303 automatic mercury electrode was employed. In those cases a single compartment cell

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[1] Gould, E. S. *J. Am. Chem. Soc.* **1965**, *87*, 4730; **1967**, *89*, 5792. Dockal, E. R.; Gould, E. S. *Ibid.* **1972**, *94*, 6672.

[2] Wu, M.-Y.; Paton, S. J.; Fanchiang, Y. T.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 326.

[3] Sprecker, H.; Wieghardt, K. *Inorg. Chem.* **1977**, *16*, 1290.

[4] (a) Dunne, T. G.; Hurst, J. K. *Inorg. Chem.* **1980**, *19*, 1152. (b) The equilibrium constant given in ref 4a was written as $(Cr(pzH)^{3+})/(Cr^{2+})(pzH^+) = 1.5 \times 10^4\ M^{-1}$; the value assigned to reaction 3 was calculated by taking $K_a = (pz)(H^+)/(pzH^+) = 0.25$.[4a]

[5] Jones, J.; Anson, F. C. *Inorg. Chem.* **1969**, *8*, 195. Barclay, D. J.; Passeron, E.; Anson, F. C. *Ibid.* **1970**, *9*, 1024.