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Contribution from the Institut für Anorganische Chemie,
Universität Bern, CH-3000 Bern 9, Switzerland

Synthesis and Spectroelectrochemical Properties of Pentaammineruthenium(II) Complexes of Quinone Diimines

K. RIEDER, U. HAUSER, H. SIEGENTHALER, E. SCHMIDT, and A. LUDI*

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Reported are the syntheses and spectral characterizations of a series of ruthenium(II) complexes of the type $(NH_3)_5Ru^{II}L^{n+}$, where the ligand L represents the *p*-quinone diimine of *p*-phenylenediamine, 1-amino-4-dimethylaminobenzene, 1,4-diaminonaphthalene, and *p*-aminophenol. The stabilization of the various benzoquinone diimines by complexation to pentaammineruthenium(II) is accompanied by a greatly enhanced basicity of the ligand. For *p*-benzoquinone diimine, the pK_a of the free ligand is 5.75, whereas a value of 10.6 is determined for the corresponding ruthenium complex. The electronic spectra of all of the complexes are characterized by an intense (log $\epsilon \approx 4.5$) band at about 18 kK. Deprotonation causes a shift of this band toward smaller energies. This absorption band is assigned to a ligand-to-metal charge transfer, the excited state of the complex having a smaller basicity than the ground state. The results of spectroelectrochemical measurements of a number of these complexes are reported. Potential cycling between −500 and +150 mV vs. SCE corresponds to the two-electron process ruthenium(II) diimine ⇄ ruthenium(II) diamine.

The syntheses and electronic properties of a variety of mono- and binuclear complexes of ruthenium(II) pentaammine with heterocyclic nitrogen donors have been reported.[1-4] Primary amines, i.e., molecules lacking π-accepting properties, however, have not been used systematically as ligands. Only a few transition metal complexes containing the chelating ligand *o*-phenylenediamine have been described.[5] In particular, a thorough study of the five-membered series of one-electron oxidation–reduction reactions of bis(*o*-phenylenediamine)metal complexes has been reported. The terminal oxidized product of this series represents the bis(*o*-benzoquinone)metal complex.[6] A recent single-crystal X-ray study demonstrated the presence of the bidentate ligand *o*-benzoquinone diimine in the complex ion $[Fe(CN)_4C_6H_4(NH)_2]^{2-}$.[7] On the other hand the ligand behavior of *p*-phenylenediamine has been studied only very rarely. A dark blue product was described as the result of the reaction of pentacyanoammineferrate(III) with *p*-phenylenediamine.[8] This product was formulated as the binuclear complex $[(CN)_5FeHNC_6H_4NHFe(CN)_5]^{6-}$ without specifying the electronic structure of the bridging ligand. In particular it has not been clarified whether the ligand has to be described as the partially deprotonated diamine, as the *p*-benzoquinone diimine, or as a radical ion. The coordinating properties of the corresponding oxygen compounds, hydroquinone and *p*-benzoquinone, have been studied in the case of the reaction of pentacyanocobaltate(II) with *p*-benzoquinone. In the binuclear species $[(CN)_5CoOC_6H_4OCo(CN)_5]^{6-}$ the bridging ligand is represented by the dianion of hydroquinone. An unstable decomposition product contains *p*-quinone as a ligand.[9] The redox properties of *p*-phenylenediamine and related compounds have been investigated by studying their reactions with the hexacyanoferrate(II)–hexacyanoferrate(III) couple.[10]

In the course of our studies of mixed-valence complexes[11] we became interested in *p*-phenylenediamine as a possible bridging ligand in binuclear ruthenium–ammine complexes. As a first step suitable mononuclear complexes have to be synthesized. The electronic spectra of these compounds should provide information concerning the electronic structure of the ligand molecule. Preliminary experiments led to the conclusion that the extremely reactive *p*-benzoquinone diimine is stabilized by coordination to pentaammineruthenium(II). A spectroelectrochemical study has been carried out in order to correlate the optical and redox properties of the pentaammineruthenium–*p*-phenylenediamine system.

Experimental Section

Reagents. Chloropentaammineruthenium(III) chloride[12] was prepared from hexaammineruthenium(III) chloride (Johnson Matthey). Silver(I) trifluoroacetate was obtained by dissolving silver(I) oxide in the stoichiometric amount of trifluoroacetic acid and evaporating to dryness. *p*-Phenylenediamine (Fluka, Puriss) was further purified by vacuum sublimation at 140°. 1-Amino-4-dimethylaminobenzene (*N*,*N*-dimethyl-4-aniline) and *p*-aminophenol were purchased from Fluka and used without further purification. 1,4-Diaminonaphthalene was obtained from Sandoz AG, Basel, Switzerland.

Analyses. Ruthenium was determined colorimetrically.[13] C, H, and N microanalyses were carried out by the Microanalytical Laboratory of ETH, Zürich, Switzerland.

Syntheses. (*p*-Benzoquinone diimine)pentaammineruthenium(II) Hexafluorophosphate (I). A 0.100-g amount of $[Ru(NH_3)_5Cl]Cl_2$ (0.342 mmol) and 0.151 g of $AgCF_3COO$ (0.684 mmol) were covered with 3 ml of water. This mixture was kept at 50° until AgCl had coagulated. After cooling to room temperature AgCl was removed by filtration and 0.110 g of *p*-phenylenediamine (1.2 mmol) was added. After a few minutes the solution had an intense violet color. This solution was kept at room temperature for 12 hr and then given in small portions on a chromatography column (cellulose, Merck). Elution with methanol–0.5 *M* HCl (7:3) gave three fractions. The first band consists of the violet main product followed by a bright blue band. The third component appears as a very small blue band. The violet main fraction was evaporated to dryness on a Rotavap and redissolved in the minimal amount of water. Precipitation with ammonium hexafluorophosphate gave small violet needles with a greenish metallic luster. Identical products were obtained by the reaction of $(NH_3)_5RuH_2O^{2+}$ [3] with *p*-phenylenediamine under argon and subsequent oxidation by air. Anal. Calcd for I: C, 9.9; N, 13.5; H, 3.02; Ru, 13.9. Found: C, 9.5; N, 13.5; H, 3.31; Ru, 14.1.

(*p*-Dimethylbenzoquinone diimine)pentaammineruthenium(II) Hexafluorophosphate (II). The same procedure was applied as for the preparation of I. Because paper chromatograms showed the violet solution to consist of only one colored product, no purification by column chromatography was carried out. Precipitation with hexafluorophosphate gave violet needles with a green metallic luster which were recrystallized from water. Anal. Calcd for II: C, 12.7; N, 13.0; H, 3.46; P, 12.3; Ru, 13.4. Found: C, 12.8; N, 13.1; H, 3.45; P, 12.4; Ru, 12.7.

(1,4-Naphthoquinone diimine)pentaammineruthenium(II) Hexafluorophosphate (III). To a solution of $Ru(NH_3)_5Cl^{2+}$ (cf. preparation of I) a threefold excess of 1,4-diaminonaphthalene was added. The resulting deep blue solution was kept at room temperature for 12 hr. Paper chromatography showed only one colored component. Addition of ammonium hexafluorophosphate precipitated a dark blue powder which was recrystallized from water. Anal. Calcd for III: Ru, 13.0. Found: Ru, 13.2.

(*p*-Benzoquinone imine)pentaammineruthenium(II) Hexafluorophosphate (IV). To the solution of $Ru(NH_3)_5Cl^{2+}$ (cf. preparation of I) 0.110 g of *p*-aminophenol (1.2 mmol) was added. The deep violet solution was filtered after standing at room temperature for 12 hr to remove polymerization products of the excess ligand. A paper chromatogram showed only one colored species. The solid compound having the same appearance as I was precipitated by adding ammonium hexafluorophosphate and recrystallized from water. Analytical and electrical conductivity data show that IV is always partially protonated. Therefore the relative proportions rather than the absolute values of Ru, C, N, and H are considered to be meaningful. Anal. Calcd for IV (or (IV)H$^+$): C:N:H = 6:6:20 (6:6:21). Found: C:N:H = 5.98:6:19.75.

(*p*-Phenylenediamine)pentaammineruthenium(II) Hexafluorophosphate (V). The ion $Ru(NH_3)_5Cl^{2+}$ (cf. preparation of I) was reduced with freshly prepared zinc amalgam in the presence of a fivefold excess of *p*-phenylenediamine. The resulting yellow solution was filtered from the zinc amalgam into a saturated solution of NH_4PF_6 giving a yellow precipitate. All operations were carried out under argon. The yellow *p*-phenylenediamine complex is rapidly oxidized to the violet compound I upon exposure to air. Anal. Calcd for V: Ru, 13.8. Found: Ru, 13.8.

Physical Methods. Spectra. Ultraviolet–visible solution spectra were measured at room temperature on a Cary 17 recording spectrophotometer. A HP 9830 A calculator together with a HP 9864 A digitizer and a HP 9862 A plotter has been used to generate the spectra presented in Figures 2 and 3 from the original Cary 17 recordings.

Spectroelectrochemistry. A transparent thin-layer cell[14] provided the possibility for both coulometric and in situ spectroscopic investigations of redox phenomena during controlled-potential electrochemical oxidation or reduction.

This spectroelectrochemical assembly is presented schematically in Figure 1. A conventional quartz flow cell with an optical path length of 0.2 mm was equipped with a gold minigrid (500 lines/in., transparency ca. 60%; Buckbee Mears Co., St. Paul, Minn.). This minigrid operates as the working electrode in a potentiostatic circuit consisting of a Philbrick P85AU operational amplifier (potentiostat) and a Radiometer Polariter PO4 polarograph (linear voltage source and current recorder). Electrochemical connection between the thin layer and the bulk electrolyte compartment (reference vessel) containing counterelectrode (Pt wire) and the reference electrode (calomel electrode in saturated sodium chloride solution) is maintained by means of a capillary tube. The thin-layer compartment can be filled from a storage tank by applying gas pressure out of the argon supply system used for deaerating the electrolyte.

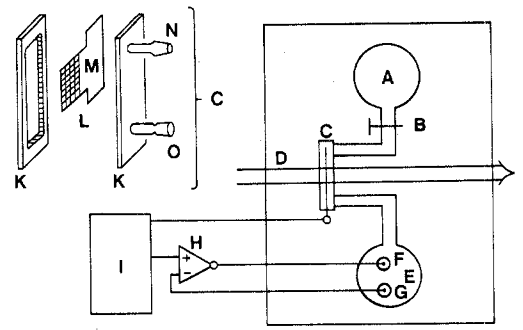


Figure 1. Diagram of the spectroelectrochemical assembly with an exploded view of the thin-layer cell: A, storage tank; B, stopcock; C, thin-layer cell; D, sample beam; E, reference vessel; F, counterelectrode (Pt); G, reference electrode (SCE); H, potentiostat; I, polarograph; K, quartz cell, optical path length 0.2 mm; L, gold minigrid; M, aluminum foil; N and O, connections to storage and reference vessels, respectively.

The uncompensated electrolyte resistance across the capillary between the thin-layer and the bulk electrolyte compartment was in the range of 3–4 kilohms. The resulting current-dependent potential drop causes a cathodic or anodic distortion of the potential axis which has not been corrected in the present results. Diffusional transport between the bulk electrolyte compartment and the thin layer has been shown to be negligible within the time of an experiment (ca. 20 min).

The electrochemically active volume V_{eff} of the thin-layer cell was determined by coulometric evaluation of cyclic voltammograms of the $Fe(CN)_6^{3-}$–$Fe(CN)_6^{4-}$ couple between −200 and +600 mV vs. SCE, using a 5.1×10^{-4} *M* solution of $K_4Fe(CN)_6$ in 1 *M* $NaClO_4$. Cell volumes were in the order of magnitude of 3×10^{-2} cm^3.

The complexes were dissolved in the supporting electrolytes listed in Table IV in the concentration range (6–7.5) $\times 10^{-4}$ *M*. The solutions were deaerated in the spectroelectrochemical assembly for ca. 1 hr with purified argon.

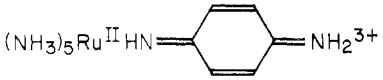
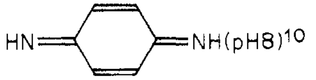
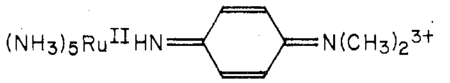
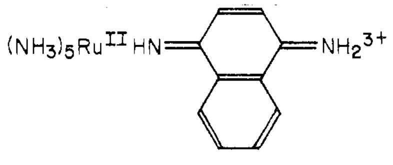
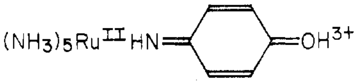
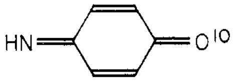
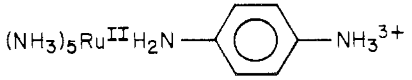
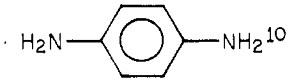
The whole assembly is mounted on a PVC plate and placed in the thermostated (25 ± 0.1°) sample compartment of the Cary 17 spectrophotometer. Spectra can be conveniently recorded in the wavelength range 1500–200 nm.[11] Typical scan rates for the linear potential sweep were in the order of 0.1 V/min.

Magnetic Susceptibilities. Magnetic susceptibilities of I and II were measured on the susceptibility balance of the Inorganic Laboratory of ETH, Zürich, and on a Bruker Minisusi in the temperature range 77–300 K.

Results and Discussion

Ligand Structure and Stoichiometry. The analytical data in conjunction with the titrations of ion-exchanged solutions demonstrate that compounds I–III are 1:3 electrolytes. Compound IV shows a behavior intermediate between 1:2 and 1:3. The intensely colored crystalline complexes obtained as reaction products of the aromatic diamines with either $Ru(NH_3)_5Cl^{2+}$ or $Ru(NH_3)_5H_2O^{2+}$ and with subsequent oxidation are completely stable in air. Also the corresponding aqueous solutions appear to be quite stable since their absorption spectra do not change over a period of 1 week. Three possible structures of the ligand molecules have to be considered in combination with either ruthenium(II) or ruthenium(III): (i) the unchanged aromatic diamine, (ii) a semiquinone or Wurster type radical ion, and (iii) the quinone diimine. A preliminary ESR measurement[15] did not show any signals to be assigned to a radical species ii. The determination of the magnetic susceptibility of the solid complexes reveals diamagnetic behavior. These facts are taken as strong evidence that our compounds contain low-spin ruthenium(II). Structure i is ruled out since neither pentaammineruthenium(II) nor pentaammineruthenium(III) complexes with primary amines have intense absorption bands in the visible region. The coordination of ruthenium(II) to good π acceptors, however, gives rise to strong charge-transfer bands.[1,2] Only structure

Table I. Visible and Ultraviolet Spectra of Pentaammineruthenium(II) Complexes of Benzoquinone Imines

Complex	ν_{max}, cm^{-1} (log ϵ_{max})		
	19,150 (4.61)	25,300 sh (3.34) 26,700 (3.39) 32,300 (3.40)	38,300 (3.58)
		31,100 (2.56)	38,900 (4.43) 37,700 (4.42)
	17,600 (4.51)	23,200 sh (3.12) 25,600 (3.20) 32,200 (3.18)	38,000 (3.64)
	16,700 (~4.3)	24,100 sh 26,000 sh 30,100	38,000
	21,100 (4.6)	30,600 (3.4) 36,200 (3.6)	40,320 (3.6)
			39,500 (4.38) 38,500 (4.39)
		25,400 (2.15)	33,300 (3.40) 41,700 (3.95)
			33,100 (3.30) 41,800 (3.97)

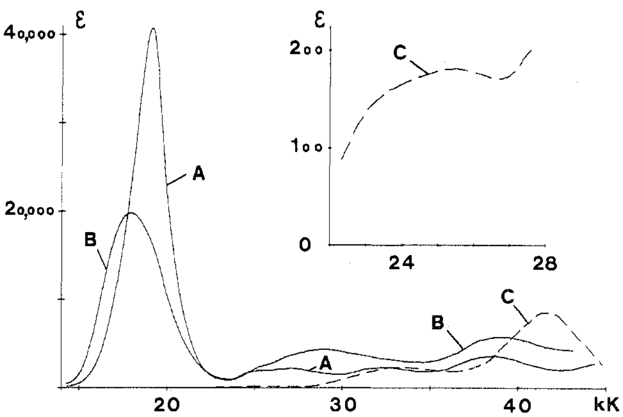
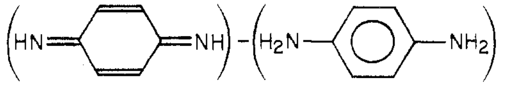
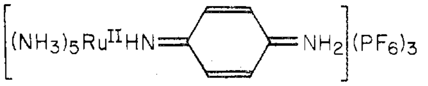


Figure 2. Absorption spectra of $(NH_3)_5Ru^{II}L$ in aqueous solution: A, L = $HN(cC_6H_4)NH_2^+$ (cC_6H_4 = 2,5-cyclohexadiene-1,4-diylidene throughout); B, L = $HN(cC_6H_4)NH$; C, L = $H_2N(C_6H_5)$-NH_3^+.

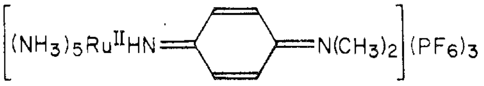
iii is in agreement with all these observations. The deeply colored compounds I–IV represent therefore pentaammineruthenium(II) complexes with the aromatic diamines in their oxidized form, i.e., with quinone diimines. In all cases the quinone diimines or quinone imines are extremely unstable species in aqueous solution hydrolyzing very rapidly to the corresponding quinone. The considerable stabilization of these molecules by complexation to ruthenium(II) may be attributed to the pronounced π-back-bonding tendency of this metal ion.[4] On the other hand the formation of this coordination compound has a great influence on the reduction potentials by considering the values of 0.10 V for the $Ru(NH_3)_6^{3+}$–$Ru(NH_3)_6^{2+}$ couple[4] and 0.45 V (pH 6) for the



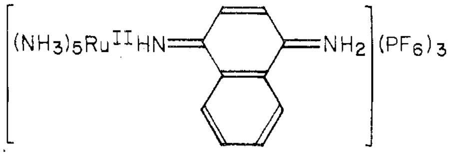
couple.[10] Finally the various analytical data show the terminal imino group to be present in its protonated form indicating an increase of the basicity of ligand molecule upon coordination (cf. Protonation Equilibria section). Thus the structures shown are assigned to compounds I–IV.



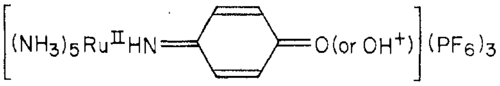
I



II



III

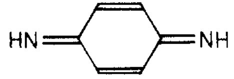
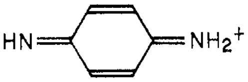
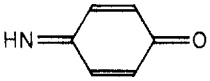
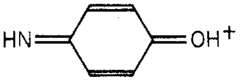


IV

Spectral Characteristics. The absorption spectra (Figure 2, Table I) of the four different complexes present the same general pattern. The dominating feature is a very intense band (log ε ≈ 4.5) between 16,000 and 20,000 cm^{-1}. An intense absorption (log ε ≈ 3.6) is observed around 38,000 cm^{-1} and two or three bands of medium intensity (log ε ≈ 3.2) appear between 23,000 and 33,000 cm^{-1}. By comparison with reported data[10] the 38,000-cm^{-1} band is assigned to an inner ligand π → π* transition.

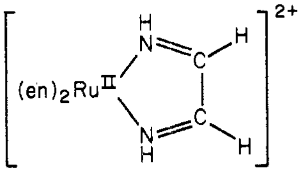
The origin of the bands between 23,000 and 33,000 cm^{-1}

Table II. Position of the Charge-Transfer Band in Protonated and Deprotonated Complexes $(NH_3)_5RuL^{2+}$

L	ν_{max}, cm^{-1} ($\log \epsilon_{max}$)	$\Delta\nu$, cm^{-1}	pK_a of the complex
	17,800 (4.24)	1350	
	19,150 (4.61)		10.6
	19,000 (4.5)	2100	
	21,100 (4.6)		2

is not very obvious. Their intensity is not compatible with an assignment as ligand field bands which are observed in this spectral region for various ruthenium(II)–ammine complexes.[2] Therefore the absorption maxima of these bands will be reported in this paper without discussing their physical origin.

The intensity of the dominating absorption band around 18,000 cm^{-1} clearly indicates that it is due to a charge transfer mechanism. As a first approximation an electron transfer either from metal to ligand or from ligand to metal has to be considered. The only other complex bearing some resemblance to these quinone diimine complexes is the oxidation product of tris(ethylenediamine)ruthenium(II) which was shown to contain one ethylenediimine molecule



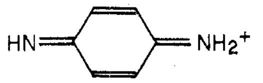
This ethylenediimine complex is reported to have an intense ($\log \epsilon = 3.85$) band at 22,300 cm^{-1} but no interpretation of this transition is offered.[16] The charge-transfer band of the quinone diimine complexes is discussed in the following section.

Protonation Equilibria. A reversible shift in position and intensity of the visible charge-transfer band is observed when the pH of the solutions of the complexes is changed. No such effect is observed for compound II where the two methyl groups at the terminal nitrogen do not allow a protonation equilibrium. In the case of the naphthoquinone diimine complex (compound III) the acid–base reaction is accompanied by a decomposition of the complex. (See Table II and Figure 3.)

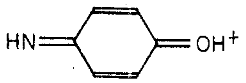
The equilibrium constant of the reaction

$$(NH_3)_5RuLH^{3+} \rightleftarrows (NH_3)_5RuL^{2+} + H^+$$

was determined by spectrophotometric titration (in 0.2 M KCl).[17] A value of 5.75 is reported for the pK_a of the free-ligand species[10]



For the corresponding complex the pK_a was determined to be 10.6 from spectrophotometric measurements, demonstrating an increase of the basicity of the terminal imino group by 5 orders of magnitude. No value is reported for the pK_a of



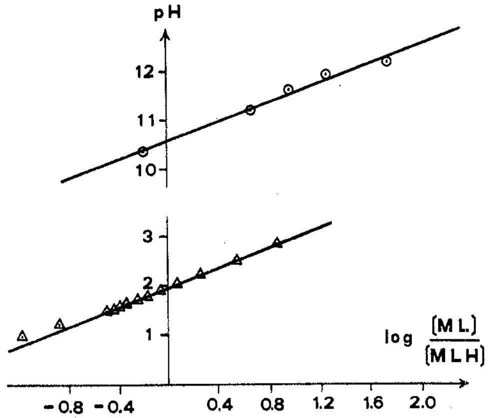
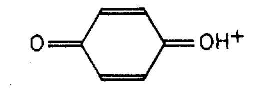
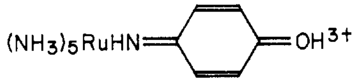


Figure 3. Protonation equilibrium $(NH_3)_5Ru^{II}L^{2+} \rightleftarrows (NH_3)_5Ru^{II}LH^{3+}$ (spectrophotometric determination using the absorption maxima given in Table II): ○, L = $HN(cC_6H_4)NH$; △, L = $HN(cC_6H_4)O$.

The acid



with $pK_a = -1.0$[10] may be considered for the purpose of comparison to the complex ion

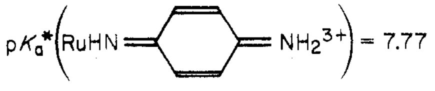


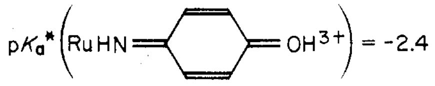
A value of 2 has been determined for the pK_a of this complex.

The charge-transfer energies can be used for the discussion of the electron-transfer mechanism, i.e., whether this intense band is due to a metal to ligand or a ligand to metal transfer. The pK_a of the charge-transfer excited state can be calculated from the equation[1,18]

$$pK_a^* = pK_a + \frac{2.86(\nu_1 - \nu_2)}{2.3RT}$$

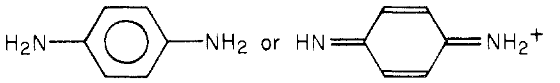
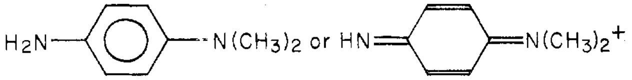
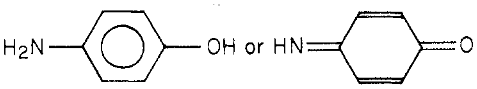
where pK_a^* is the acid dissociation constant in the charge-transfer excited state, pK_a is the acid dissociation constant in the ground state, ν_1 is the energy (cm^{-1}) of the charge-transfer absorption of the unprotonated form, and ν_2 is the energy of the corresponding absorption of the protonated molecule. A greater (smaller) basicity of the ligand after the charge transfer implies an increase (decrease) of the electron density of the ligand. It has been shown by this relation that the charge transfer corresponds to an increase of the ligand electron density of the ruthenium(II) complexes with aromatic heterocycles.[1] Consequently the visible band of these compounds was assigned to a metal → ligand electron transfer. The charge-transfer band which is observed at about 18 kK for all of the ruthenium(II)–quinone diimine complexes is shifted by about 2 kK toward smaller energies when the complexes are deprotonated. Assuming the above formula to be valid, we find, inserting the experimental values for ν_1 and ν_2 (Table II), that the excited state of the quinone diimine complexes is less basic than the ground state:





We conclude therefore that electron density is transferred from the ligand during the charge-transfer process, assigning thus the intense visible band to a ligand → metal electron transfer. The same behavior was found for the complex

Table III. Band Positions (cm^{-1}) of Ru(NH$_3$)$_5$L Complexes at Various Minigrid Potentials

L	−500 mV	+150 mV	+700 mV
	35,000 42,200	19,150 32,200 38,500	25,400 28,600 39,200
	34,400 40,600	17,600 30,300 38,000	24,000 29,900 37,200
	31,500 sh 36,100 44,800	19,500 32,300 39,200	26,300 37,000 39,700

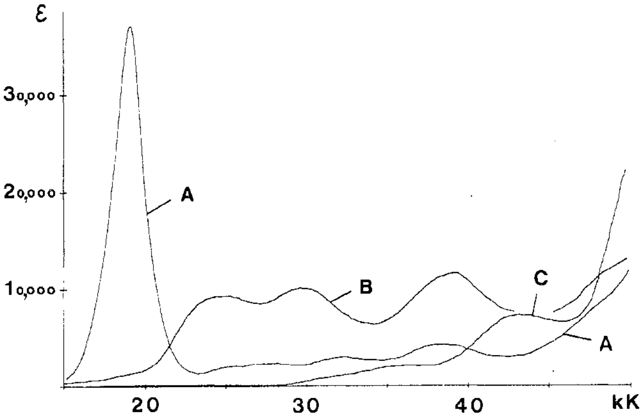


Figure 4. Absorption spectra of 6.21 × 10^{-4} *M* (NH$_3$)$_5$Ru^{II}HN-(cC$_6$H$_4$)NH$_2$$^{3+}$ at various minigrid potentials and pH 6.3: A, +150 mV; B, +700 mV; C, −500 mV.

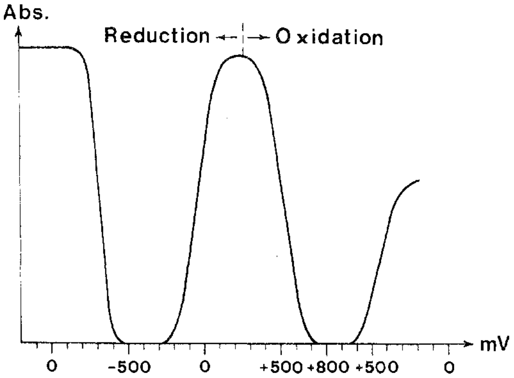


Figure 5. Plot of the absorbance at 19,150 cm^{-1} of the charge-transfer band of (NH$_3$)$_5$Ru^{II}HN(cC$_6$H$_4$)NH$_2$$^{3+}$ (6.2 × 10^{-4} *M*, pH 6.3) as a function of the minigrid potential.

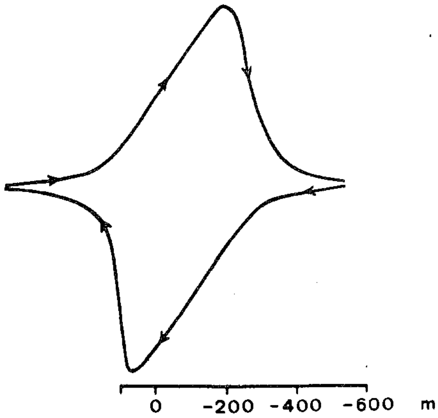


Figure 6. Cyclic voltammogram of a 7.14 × 10^{-4} *M* solution of (NH$_3$)$_5$Ru^{II}HN(cC$_6$H$_4$)NH$_2$$^{3+}$ at pH 7.9.

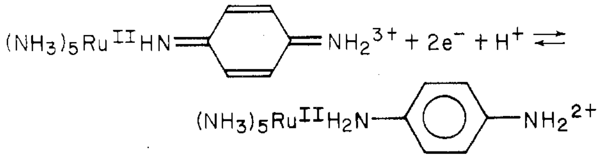
[(NH$_3$)$_4$ClOs(pyrazine)]$^+$ where protonation of the ligand leads also to a blue shift of the charge-transfer band.[19] It has to be emphasized that the assignment of this charge-transfer band to a ligand to metal electron transfer is a very crude approximation. In a better but still qualitative description the charge-transfer mechanism may be interpreted as a transition from a molecular orbital having predominantly ligand character to an excited one having predominantly metal character.

Spectroelectrochemical Properties. The correlation of redox properties of the complexes with spectral characteristics was studied by means of the spectroelectrochemical thin-layer technique.

Cyclic voltammograms of compounds I, II, and IV were recorded with linear potential sweep (scan rate 100 mV/min) in an overall potential range of +800 to −500 mV vs. SCE.

In a reduction cycle the potential was scanned cathodically from +150 mV (at this potential complexes I, II, and IV remained stable) to −500 mV followed by an anodic scan in the same potential interval.

In the case of complex I the cathodic sweep results in a well-defined reduction wave, and the spectrum recorded at the cathodic end potential (−500 mV) is identical (Table III) with that of the diamine complex of ruthenium(II) prepared under severely anaerobic conditions (compound V). Determination of the coulometric charge by integrating the voltammogram shows (Table IV) the corresponding redox reaction to be a two-electron process. Within this potential range the oxidation state of ruthenium is not affected; the redox reaction is taking place within the ligand molecule (eq 1). In the subsequent



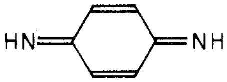
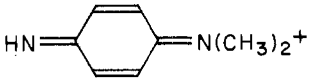
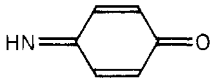
(1)

anodic branch of the voltammogram, an oxidation wave appears near the anodic potential limit of the polarizing scan. The peak potentials of the cathodic and anodic peaks differ by almost 500 mV. This large separation indicates that the electrode reaction is not only diffusion controlled but is also governed by some unknown chemical or electrochemical steps such as charge transfer at the electrode–electrolyte interphase and/or protonation of the ligand.

Nevertheless, as shown by the 95% recovery of the charge-transfer band at +150 mV vs. SCE and by the continuous spectrum recorded at the same potential, the original complex I is regenerated almost quantitatively. The charge stoichiometry calculated from coulometric analysis of the anodic scan (Table IV), however, shows deviations from the expected result which may be attributed to uncertainties in the subtraction of the residual current.

The reduction of compounds II and IV follows the same general reaction (Tables III, IV). The results for the cathodic scans (Table IV) are within the limits of confidence of 5% assigned to the coulometric evaluation of cyclic voltammograms.[14] The experimentally determined charge stoichiometry

Table IV. Redox Data of $(NH_3)_5Ru^{II}L$ Complexes

	pH	% absorbance of charge-transfer band after 1 redox cycle	Concn × 10^4, *M*	No. of electrons	
				Cathodic sweep	Anodic sweep
	7.9[a]	95	7.4	1.87	1.58
	6.3[a]	95	6.2	1.97	1.83
	6.3[a]	96.5	7.1	1.85	1.80
	4.9[a]	91.5	7.1	1.87	1.75
	7[b]	97	4.5	1.92	1.73
	6.3[a]	87	7.75	2.09	1.95

[a] Buffer solution prepared with 0.5 *M* KH_2PO_4 and 0.5 *M* Na_2HPO_4. [b] 0.5 *M* $NaClO_4$.

conforms to the reduction process of eq 1. No information is obtained, however, concerning the occurrence of intermediate species corresponding to a one-electron step. Optical monitoring in the wavelength region where the semiquinone radicals absorb[20] gives no evidence, during a full cyclic potential sweep between +150 and −500 mV, for the occurrence of the one-electron oxidation product of *p*-phenylenediamine. A possible first one-electron process in the oxidation of the *p*-phenylenediamine complex must be rapidly followed by a second one-electron oxidation to *p*-benzoquinone diimine. The rate of the second step has to be fast compared to the time scale of the voltammetric experiments. The same arguments hold for the two-electron reduction of the diimine to the diamine complex.

Oxidation cycles in the potential range +150 to +700 mV with quantitative or almost quantitative regeneration of the original complex can only be scanned with compound II. In the other cases after a full redox cycle only about 60% of the extinction of the charge-transfer band is again observed. The cyclic voltammograms corresponding to the oxidation of the ruthenium(II)–quinone imine complexes are obscured by the onset of an anodic slope in the voltammogram starting at about +650 mV. Therefore no reliable coulometric evaluation of the voltammograms was made and hence no definite charge stoichiometry of the oxidation process can be established. As a consequence it is also impossible unambiguously to characterize the oxidation product. The absorption spectrum (Figure 4) at +700 mV shows the absorption band at 38,000 cm^{-1} which is considered to be diagnostic for the benzoquinone diimine molecule. The oxidized forms of the complexes I, II, and IV may be considered as the benzoquinone complexes of ruthenium(III). Additional data, however, have to be collected to test this hypothesis.

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Registry No. I, 55161-88-1; II, 55162-24-8; III, 55161-92-7; IV, 55161-90-5; V, 55161-86-9; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1; *p*-phenylenediamine, 106-50-3; 1-amino-4-dimethylaminobenzene, 99-98-9; *p*-aminophenol, 123-30-8; 1,4-diaminonaphthalene, 2243-61-0.

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