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Chemistry of Ruthenium. 3. Synthesis, Structure, and Electron-Transfer Behavior of *trans*-Dihalobis[(arylazo)oximato]ruthenium(III)

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New haloruthenium(III) (arylazo)oximates of the type RuX$_2$(HL)(L) are described (X = Cl, Br; HL = RC(=NOH)-N=NAr). The RuX$_2$ moiety has trans configuration (IR data); the hydrogen-bonded organic part LHL acts essentially as a planar tetradentate ligand. In effect the coordination sphere is *trans*-RuN$_4$X$_2$. The complexes are low spin (t$_{2g}^5$, S = ^{1}/$_2$) and display characteristic EPR spectra in the polycrystalline state at room temperature as well as in frozen benzene. The spectra are sensitive to the nature of R and Ar groups and can be nearly isotropic, axial, or rhombic. The complexes show two LMCT bands near 1000 and 580 nm. They undergo a reversible one-electron transfer at the platinum electrode attributable to the ruthenium(III)–ruthenium(II) couple (cyclic voltammetry and constant potential coulometry). The $E°_{298}$ of this couple is ~0.4 V vs. SCE in acetonitrile. A bromo complex is easier to reduce than the corresponding chloro complex. The interrelationship of $E°_{298}$ with LMCT band energy is noted. The green ruthenium(II) species RuX$_2$(HL)(L)$^-$ has been generated in solution both electrochemically and chemically (reduction by hydroquinone). It has a characteristic MLCT band near 680 nm. Addition of base (NEt$_3$) deprotonates RuX$_2$(HL)(L) quantitatively to RuX$_2$(L)$_2^-$ with concomitant loss of the electrochemical response which is fully reestablished on addition of acid (HClO$_4$).

Introduction

This work which stems from our interest[1–3] in synthesis, structure, and reactivity of new ruthenium complexes concerns preparation, IR and electronic spectra, EPR response, and redox activity of ruthenium(III) chelates of (arylazo)oximes. These ligands (**1**) are known[4] to be good bidentate nitrogen
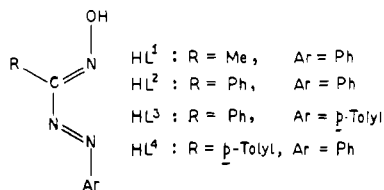
donors toward a number of transition-metal ions. Oximes in general are versatile ligands,[5] but surprisingly there are very few published reports[1,2,6,7] on ruthenium complexes of such ligands. The present study is a part of the systematic investigations that we have initiated[1,2] on such complexes. The

ligand **1** also has the azoimine fragment, N=CN=N, which is isoelectronic with the diimine fragment, N=CC=N, present in 2,2'-bipyridine whose ruthenium chemistry has been the subject matter of many recent studies.[8–10] The ligands are generally abbreviated as HL. Specific ligands are abbreviated as HL^1 to HL^4 as shown in **1**. Earlier we have briefly reported[2] some diamagnetic ruthenium(II) complexes derived from HL^1 and HL^2. The species described in the present work are prepared under entirely different conditions, and they belong to a different structural type.

Experimental Section

Materials. (Arylazo)oximes were prepared as before.[5,11] Ru-Cl$_3$·3H$_2$O was purified as described earlier.[1] Electrochemically pure acetonitrile and dichloromethane solvents and tetraethylammonium perchlorate (TEAP) were prepared[1,3] from commercial materials. For deprotonation experiments, known concentration of triethylammine solution in CH$_3$CN was prepared by directly adding a known weight of the freshly distilled amine to the CH$_3$CN solvent. Standard (~0.01 M) perchloric acid solution was prepared by adding a known amount of standardized concentrated (70% in aquous solution) acid to the CH$_3$CN solvent.

Measurements. IR spectra were recorded in KBr (4000–400 cm^{-1}) and polyethene disks (400–100 cm^{-1}) with use of Beckman IR-20A and IR-720 spectrophotometers, respectively. Electronic spectra were

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measured with a Cary 17D spectrometer. X-Band EPR spectra were recorded with a JEOL 3 × 100 spectrometer fitted with a variable-temperature cryostat. The spectra were calibrated with use of a sample of DPPH (g = 2.0036 ± 0.0003). The magnetic susceptibility was measured in a Gouy balance using $CoHg(SCN)_4$ as the calibrant. Electrochemical measurements (cyclic voltammetry, controlled-potential coulometry, and chronoamperometry) were carried out with the help of the PAR 370-4 electrochemistry system which includes the 174A polarographic analyzer, 175 universal programmer, RE 0074 X–Y recorder, 173 potentiostat, 179 digital coulometer, and 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. Microanalysis was done by CSIRO, Australia, Molecular weight determination was carried out osmometrically with use of Knauer vapor pressure osmometer.

Preparation of Complexes. The compounds were prepared by using the same general procedure. Details are given below for one chloro and one bromo complex.

Dichloro[α-(phenylazo)benzaldoximato-N,N''][α-(phenylazo)-benzaldoxime-N,N'']ruthenium(III), $RuCl_2(HL^2)(L^2)$. A 0.225-g sample (1 mmol) of HL^2 was added to a solution of 0.13 g (0.5 mmol) of $RuCl_3\cdot3H_2O$ in 10 mL of methanol containing 1 g of LiCl. The mixture was stirred for 8 h magnetically. It was then cooled to 0 °C, and the precipitated complex was collected by filtration and washed thoroughly with water and finally with 95% aqueous ethanol. The compound thus obtained was dried in vacuo over P_4O_{10} and was then dissolved in a small volume (5 mL) of CH_2Cl_2. This solution was subjected to chromatography on a silica gel column (30 × 1 cm) using benzene as the eluant. A red-violet band was thus eluted out. A very slow moving pink band remained near the top of the column. Crystals were obtained on slow evaporation of the red-violet benzene eluate at room temperature. The yield was 0.08 g (25%) (mp > 200 °C).

Anal. Calcd for $RuC_{26}H_{21}N_6O_2Cl_2$: C, 50.20; H, 3.70; N, 13.20; Cl, 11.00. Found: C, 50.21; H, 3.35; N, 13.18; Cl, 11.20.

Molecular Weight: calcd, 621; found, 600.

Dibromo[α-(phenylazo)benzaldoximato-N,N''][α-(phenylazo)-benzaldoxime-N,N'']ruthenium(III), $RuBr_2(HL^2)(L^2)$. This was prepared by the same procedure as above except that $RuCl_3\cdot3H_2O$ was stirred for 10 min with 1 g of LiBr (no LiCl was added) in 10 mL of methanol prior to the addition of HL^2. The yield was 0.09 g (25%) (mp 184 °C). Anal. Calcd for $RuC_{26}H_{21}N_6O_2Br_2$: C, 43.97; H, 3.10; N, 11.81. Found: C, 44.29; H, 3.29; N, 12.03.

Dichloro[α-(p-tolylazo)benzaldoximato-N,N''][α-(p-tolylazo)-benzaldoxime-N,N'']ruthenium(III), $RuCl_2(HL^3)(L^3)$. The yield was 0.16 g (50%) (mp > 200 °C). Anal. Calcd for $RuC_{28}H_{25}N_6O_2Cl_2$: C, 51.68; H, 4.00; N, 12.92; Cl, 10.92. Found: C, 52.10; H, 4.32; N, 12.68; Cl, 11.60.

Dibromo[α-(p-tolylazo)benzaldoximato-N,N''][α-(p-tolylazo)-benzaldoxime-N,N'']ruthenium(III), $RuBr_2(HL^3)(L^3)$. The yield was 0.19 g (59%) (mp 195 °C). Anal. Calcd for $RuC_{28}H_{25}N_6O_2Br_2$: C, 45.46; H, 3.52; N, 11.37. Found: C, 45.79; H, 3.89; N, 11.32.

Dichloro[α-(phenylazo)acetaldoximato-N,N''][α-(phenylazo)-acetaldoxime-N,N'']ruthenium(III), $RuCl_2(HL^1)(L^1)$. In this case and in the case of the bromo analogue (see below) washing by 95% aqueous ethanol and drying over P_4O_{10} gave sufficiently pure product, and chromatographic purification over silica gel was not necessary. The yield was 0.08 g (30%) (mp 155 °C dec). Anal. Calcd for $RuC_{16}H_{17}N_6O_2Cl_2$: C, 38.24; H, 3.58; N, 16.73; Cl, 14.14. Found: C, 38.60; H, 3.61; N, 16.68; Cl, 14.40.

Dibromo[α-(phenylazo)acetaldoximato-N,N''][α-(phenylazo)-acetaldoxime-N,N'']ruthenium(III), $RuBr_2(HL^1)(L^1)$. The yield was 0.09 g (25%); (mp 170 °C). Anal. Calcd for $RuC_{16}H_{17}N_6O_2Br_2$: C, 32.71; H, 2.90; N, 14.31. Found: C, 32.99; H, 3.10; N, 14.79.

Dichloro[α-(phenylazo)-p-tolualdoximato-N,N''][α-(phenylazo)-p-tolualdoxime-N,N'']ruthenium(III), $RuCl_2(HL^4)(L^4)$. The yield was 0.1 g (30%) (mp 180 °C dec). Anal. Calcd for $RuC_{28}H_{25}N_6O_2Cl_2$: C, 51.68; H, 4.00; N, 12.92; Cl, 10.92. Found: C, 52.12; H, 3.96; N, 12.44; Cl, 11.10.

Dibromo[α-(phenylazo)-p-tolualdoximato-N,N''][α-(phenylazo)-p-tolualdoxime-N,N'']ruthenium(III), $RuBr_2(HL^4)(L^4)$. The yield was 0.19 g (59%) (mp 180 °C dec). Anal. Calcd for

$RuC_{28}H_{25}N_6O_2Br_2$: C, 45.46; H, 3.52; N, 11.37. Found: C, 45.57; H, 3.68; N, 11.06.

The complexes are insoluble in water and hexane, sparingly soluble in benzene, diethyl ether, methanol, and ethanol, moderately soluble in acetonitrile and nitromethane, and highly soluble in dichloromethane, chloroform, acetone, and dimethyl sulfoxide. In a given solvent, HL^1 complexes are more soluble than those of the other ligands. Bromo complexes are in general more soluble than the chloro analogues. The complexes are uniformly nonconductors of electricity in nitromethane and acetonitrile.

Results and Discussion

A. Formulation and Structure. As elaborated in following sections, the red-violet complexes formed by facile reactions between RuX_3 and HL uniformly display one-electron paramagnetism, EPR spectra for the spin doublet ground state, LMCT transitions in the visible region, a one-electron electrochemical reduction at positive potentials, and a deprotonation reaction involving one proton. These facts taken collectively with analytical and molecular weight data lead unequivocally to the ruthenium(III) formulation $RuX_2(HL)(L)$ at the exclusion of two possible alternatives $RuX_2(HL)_2$ (ruthenium(II), two protons) and RuX_2L_2 (ruthenium(IV), no proton).

The configuration of the RuX_2 moiety is settled by far–IR data. The $RuCl_2$ species show a sharp and strong band at ~345 cm^{-1} which shifts to ~270 cm^{-1} in the $RuBr_2$ analogues. This band is evidently assignable[1,3] to RuX (Table I). The band is a singlet, and therefore the RuX_2 stereochemistry is trans. Since one ligand is present in the protonated form, careful search for ν_{OH} was made but with negative results. As discussed elsewhere,[1,5,12] this implies that the oxime hydrogen atom is engaged in strong intramolecular hydrogen bonding. Recent X-ray work[13] shows the presence of strong intramolecular O---H---O hydrogen bonding in the Cu(I) dimer $[Cu(HL^1)(L^1)]_2$ in which ν_{OH} is again not observable.[14]

All observations are in accord with the gross structure **2**

2
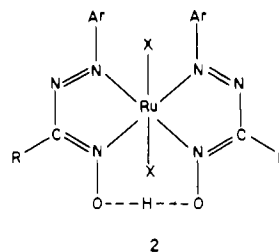
which has a *trans*-RuX_2N_4 coordination sphere. Arylazo oximes are usually bidentate and uniformly bind to metal ions through oxime and azo nitrogen atoms generating five-membered chelate rings. The formation of such rings is attended with a considerable upward shift of ν_{NO} from the free ligand value.[4] The same happens in the present complexes which display a strong ν_{NO} band at ~1270 cm^{-1} (Table I).

This cis disposition of two Ar groups in **2** is likely to have steric disadvantage compared to the possible trans disposition in an alternative structure. However, formation of the strong intramolecular O---H---O bond is possible only in the cis disposition. The energy of this bond may compensate for the repulsive steric interaction of Ar groups in **2**. An essential feature of structure **2** is the presence of a grossly planar tetradentate ligand formed by the union of two bidentate ligands via oxime–oximato O---H---O hydrogen bonding. Other than in $RuX_2(HB)(B)$[1] (HB = α-benzil oxime) this structural feature is unknown at present in dihaloruthenium chemistry.

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Table I. Selected Infrared,[a] Bulk Susceptibility,[b] and EPR[c] Data

compd	IR spectra, cm^{-1}		bulk susceptibility (298 K)	EPR data			
	ν_{NO}	ν_{RuX}	μ_{eff}, μ_B	g_1	g_2	g_3	g_{bz}[d]
RuCl$_2$(HL^1)(L^1)	1275	347	1.90	2.361	2.361	1.988	2.188
RuBr$_2$(HL^1)(L^1)	1275	270	2.08		(2.181)[e]		2.216
RuCl$_2$(HL^2)(L^2)[f]	1275	349	1.87	2.324	2.324	1.948	2.184
RuBr$_2$(HL^2)(L^2)	1270	270	1.86	2.419	2.419	2.039	2.216
RuCl$_2$(HL^3)(L^3)[g]	1268	346	1.90	2.310	2.228	2.020	2.189
RuBr$_2$(HL^3)(L^3)	1265	272	1.87	2.369	2.261	2.030	2.236
RuCl$_2$(HL^4)(L^4)	1268	343	1.97		(2.201)[e]		2.177
RuBr$_2$(HL^4)(L^4)	1270	264	1.85		(2.208)[e]		2.223

[a] In KBr disk (4000–400 cm^{-1}) and in polyethene disk (400–100 cm^{-1}). [b] Gouy method using CoHg(SCN)$_4$ as standard. [c] Polycrystalline sample at 298 K. [d] In benzene at 298 K. [e] Only average spectrum is observed. [f] In frozen benzene at 123 K, g_1, g_2, and g_3 are 2.319, 2.319, and 1.932, respectively. [g] In frozen benzene at 153 K, g_1, g_2, and g_3 are 2.313, 2.230, and 2.135, respectively.

Table II. Electronic Absorption Spectral Data[a,b] at 298 K

complex	solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})			
RuCl$_2$(HL^1)(L^1)	CH$_2$Cl$_2$	955 (380)	550 (3300)		370 (10 100)
RuBr$_2$(HL^1)(L^1)	CH$_2$Cl$_2$	970 (420)	550 (4780)		372 (12 900)
RuCl$_2$(HL^2)(L^2)	CH$_2$Cl$_2$	1024 (970)	580 (8730)	530^c	376 (15 600)
	CHCl$_3$	1035 (1010)	580 (8630)	520^c	375 (15 400)
	CH$_3$CN	1030 (930)	575 (9100)		375 (16 500)
	CH$_3$COCH$_3$	1010 (980)	580 (8240)	520^c	375 (15 100)
	CH$_3$NO$_2$	1020 (840)	576 (8150)		375 (15 800)
RuBr$_2$(HL^2)(L^2)	CH$_2$Cl$_2$	1042 (1030)	582 (8150)	550 (7720)^d	374 (13 700)
RuCl$_2$(HL^3)(L^3)	CH$_2$Cl$_2$	1035 (940)	582 (9910)	560^c	385 (16 400)
RuBr$_2$(HL^3)(L^3)	CH$_2$Cl$_2$	1050 (750)	580 (7740)^d	526 (8290)	383 (14 700)
RuCl$_2$(HL^4)(L^4)	CH$_2$Cl$_2$	1045 (1010)	588 (9030)	560^c	375 (14 400)
RuBr$_2$(HL^4)(L^4)	CH$_2$Cl$_2$	1070 (1080)	590 (8760)	550 (8340)^d	366 (14 300)
RuCl$_2$(L^2)$_2$$^-$	CH$_3$CN	1045 (1230)	540 (5200)^e	495 (7720)^e	g
RuCl$_2$(HL^1)(L^1)$^-$	CH$_3$CN		670 (4500)		352^c
RuBr$_2$(HL^1)(L^1)$^-$	CH$_3$CN		660 (5700)	480^c	352 (9600)^d
RuCl$_2$(HL^2)(L^2)$^-$	CH$_3$CN		690 (8500)	500^c	345 (16 300)
RuBr$_2$(HL^2)(L^2)$^-$	CH$_3$CN		675 (9000)	490^c	335 (16 700)
RuCl$_2$(HL^3)(L^3)$^-$	CH$_3$CN		684 (8000)		352 (15 000)
RuBr$_2$(HL^3)(L^3)$^-$	CH$_3$CN		673 (6000)^f	g	g
RuCl$_2$(HL^4)(L^4)$^-$	CH$_3$CN		682 (8500)	488^c	342 (16 000)^d
RuBr$_2$(HL^4)(L^4)$^-$	CH$_3$CN		676 (7000)^f	g	g

[a] RuCl$_2$(L^2)$_2$$^-$ is the deprotonated species obtained by adding base (NEt$_3$) to the solution of RuCl$_2$(HL^2)(L^2) (see text). [b] RuX$_2$(HL)(L)$^-$ species were obtained by coulometric reduction of RuX$_2$(HL)(L) complexes in acetonitrile at 0.0 V or by chemical reduction using hydroquinone as reducing agent (see text). [c] Shoulder, not well resolved. [d] Shoulder, well resolved. [e] Broad. [f] Solutions are not stable. [g] Not measured.

B. Magnetic Susceptibility and EPR Spectra.

The room-temperature magnetic susceptibility of every complex shows the presence of one unpaired electron (Table I). The complexes are thus low spin (t$_{2g}^5$) in character. In such species spin-lattice relaxation is usually rapid, and it is necessary to go to low temperature for observing EPR spectra. This is not so in the case of **2** which display characteristic resonance signals at room temperature in the polycrystalline phase (Figure 1). In a few cases studied such spectra are essentially the same as those in frozen benzene. Observed **g** tensors evaluated by a published method[15] lie in the range 1.9–2.4. The spectra are surprisingly sensitive to the nature of R and Ar and can be rhombic, axial, or nearly isotropic (Table I). Earlier we have noted the possible existence of a balance between Ar···Ar repulsion and O---H---O hydrogen bonding in **2**. If this balance is somewhat critical, change of substituent can bring about effective changes in the ground-state symmetry as observed in EPR spectra. The sign and magnitude of **g** tensors of low-spin d^5 pseudooctahedral complexes depend on the orbital composition of the ground Kramers doublet.[16-20]
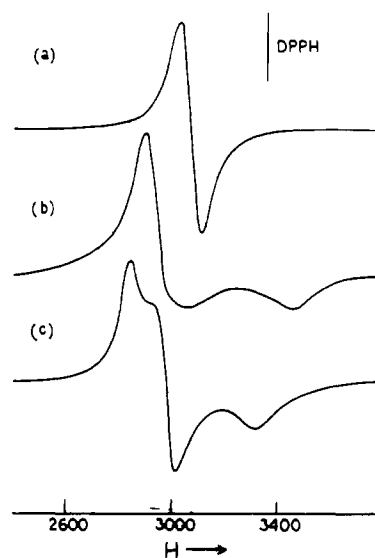

Figure 1. Room-temperatures EPR spectra: (a) benzene solution of RuCl$_2$(HL^4)(L^4); (b) polycrystalline RuCl$_2$(HL^2)(L^2); (c) polycrystalline RuBr$_2$(HL^3)(L^3).

This composition inturn depends on tetragonal and rhombic distortion parameters, the orbital reduction parameter, and

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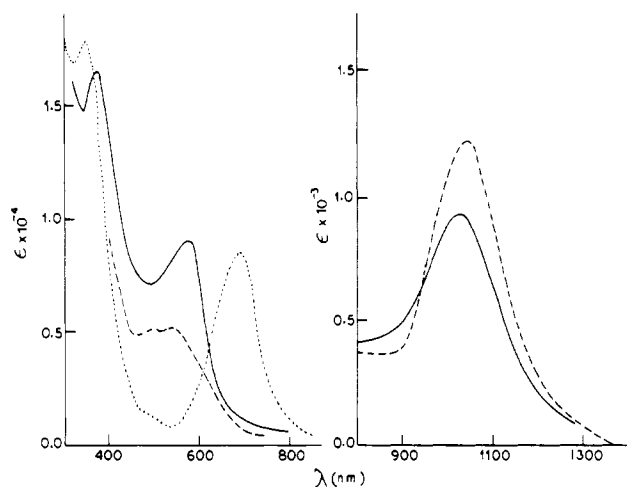(19) Cotton, S. A.; Gibson, J. F. *J. Chem. Soc. A* **1971**, 803.

Figure 2. Electronic spectra in acetonitrile solution: —, RuCl₂-(HL²)(L²); ---, RuCl₂(L²)₂⁻; ⋯, RuCl₂(HL²)(L²)⁻.

the spin–orbit coupling constant.[18] A complete analysis of the EPR spectra of **2** and closely related complexes in terms of these parameters will be reported shortly.

C. Electronic Spectra. Electronic spectra of red-violet solutions of RuX₂(HL)(L) were scanned in the region 1500–300 nm. Several bands are observed (Table II, Figure 2). In general, intensities of bands are greater when the R group of ligand (**1**) is aryl (HL²–HL⁴) than when the R is alkyl (HL¹). The most distinctive feature of the spectra is a relatively strong band at ∼1000 nm. Presence of moderately intense (ε ≈ 10²–10³) low-energy band(s) in ruthenium(III) complexes are not unknown:[21,22] Ru(bpy)₃³⁺, 676 nm (ε = 409); RuCl(PPh₃) (salen), 737 nm (ε = 5956); Ru(bpy)₂-(Ph₂PCH=CHPPh₂)³⁺, 840 nm (ε = 126) [where bpy = 2,2′-bipyridine, salen = N,N′-ethylenebis(salicylaldiminate)]. In α-benzil oximato species, RuX₂(HB)(B), a band appears at ∼775 nm (ε ≈ 350) though it was not reported[1] earlier. To our knowledge the band position of the arylazo oximates is lowest in energy among reported ruthenium(III) complexes. We believe that this band is due to ligand (π) → metal (t₂g) charge-transfer (LMCT) transition. For a given HL, this LMCT band systematically has the energy order Cl > Br. Thus the t₂g level is lower in the bromo complex, suggesting that decrease of metal–ligand π interaction is less in the chloro complex. One or two other intense bands are observable in the 500–600-nm region. These may also be LMCT bands originating from more stable ligand orbitals. The position of both the ∼1000- and ∼580-nm band positions are solvent dependent (Table II). A ligand-centered band near 375 nm appears in all the complexes.[11] In chloro and bromo complexes of ruthenium(III), the X → Ru charge-transfer band is known to appear at ≤400 nm. The X = Cl and X = Br bands are separated[22,23] by nearly 5000 cm⁻¹. Such bands could not be located in the present complexes possibly due to overlap with other more intense bands. In the case of Ru(bpy)₂(PR₃)Cl²⁺ complexes a band near 600 nm has been assigned[24] to the Cl → Ru transition. It will be shown elsewhere that this band is actually due to a bpy (π*) → Ru (t₂g) transition.

D. Redox Activity. The complexes **2** display two stages of reduction at the platinum working electrode. The one that definitely involves the metal ion is discussed below in detail.

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Table III. Electrochemical Data[a] for the Complexes RuX₂(HL)(L) at the Platinum Electrode (298 K)

complex	solvent[b]	v, mV s⁻¹	$E°_{298}$, V (ΔE_p, mV) Ru(III)–Ru(II)	ligand redn[c]	$10^5 D$, cm² s⁻¹
RuCl₂(HL¹)(L¹)	CH₃CN	20–100	0.39 (60)	−0.83	1.46
		200	0.39 (65)		
	CH₂Cl₂	20	0.31 (118)	d	1.02
		100	0.31 (180)		
RuBr₂(HL¹)(L¹)	CH₃CN	20–100	0.42 (70)	−0.85	
		200	0.42 (75)		
	CH₂Cl₂	20	0.33 (148)	d	
		100	0.33 (237)		
RuCl₂(HL²)(L²)[e]	CH₃CN	20–100	0.48 (65)	−0.78	1.14
		200	0.48 (70)		
	CH₂Cl₂	20	0.41 (123)	d	1.08
		100	0.41 (185)		
RuBr₂(HL²)(L²)	CH₃CN	20–100	0.52 (65)	−0.73	
		200	0.52 (70)		
	CH₂Cl₂	20	0.42 (143)	d	
		100	0.42 (230)		
RuCl₂(HL³)(L³)	CH₃CN	20–100	0.45 (60)	−0.81	0.93
		400	0.45 (65)		
	CH₂Cl₂	20	0.36 (128)	d	0.83
		100	0.36 (200)		
RuBr₂(HL³)(L³)	CH₃CN	20–50	0.47 (60)	−0.88	
		100	0.47 (65)		
	CH₂Cl₂	20	0.38 (135)	d	
		100	0.38 (210)		
RuCl₂(HL⁴)(L⁴)[f]	CH₃CN	20–100	0.44 (60)	−0.83	0.79
		400	0.44 (65)		
	CH₂Cl₂	20	0.37 (127)	d	0.64
		100	0.37 (210)		
RuBr₂(HL⁴)(L⁴)	CH₃CN	20–100	0.46 (60)	−0.85	
		400	0.46 (70)		
	CH₂Cl₂	20	0.40 (105)	d	
		100	0.40 (160)		

[a] Meaning of symbols are same as in text. [b] Supporting electrolyte TEAP (0.1 M), solute concentration ∼10⁻³ M. [c] Cathodic peak potential (E_{pc} in V). [d] Not studied. [e] Coulometry (8.0 mg of complex exhaustively reduced at 0.0 V): calcd, Q = 1.24 C; found, Q = −1.22 C. [f] Coulometry (5.1 mg of complex exhaustively reduced at 0.0 V): calcd, Q = 0.76 C; found, Q = −0.75 C.

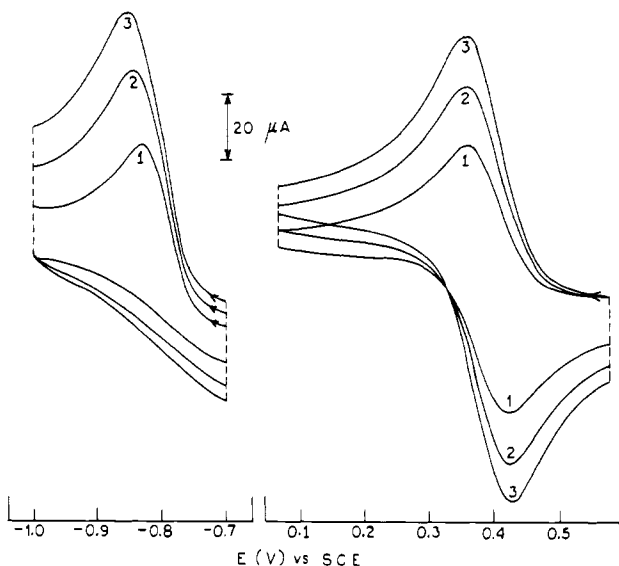**Figure 3.** Cyclic voltammograms (platinum electrode) of RuCl₂-(HL¹)(L¹) in CH₃CN (0.1 M TEAP) at different scan rates: (1) 50 mV s⁻¹, (2) 100 mV s⁻¹, (3) 150 mV s⁻¹.

A second reduction occurring near −0.8 V vs. SCE (Figure 3, Table III) is essentially irreversible with nearly zero response on the anodic scan. It is believed that this reduction involves

the azo function of the ligands. A reduction in similar position occurs systematically in many transition-metal complexes of (arylazo)oximes and other azo ligands.[3,25-28] This reduction will not be considered any further.

(a) One-Electron Electrochemical Reduction of Ruthenium-(III). Near 0.45 V well-defined cathodic and anodic cyclic voltammetric peaks of equal height are observed (Figure 3). The process was studied over the range of scan rates (v) 20–500 mV s^{-1}. At slow scan rates. (v < 100 mV s^{-1}) in acetonitrile the peak-to-peak separation, ΔE_p, lies in the range 60–70 mV (Table III) showing that the process is reversible or nearly reversible and involves one-electron transfer. In constant-potential experiments (stirred solution) electrolysis was found to occur freely when the potential of the working electrode was fixed on the negative side of the cathodic peak. At potentials more than that of the anodic peak no electrolysis occurred. Thus **2** is undergoing reduction and not oxidation. Constant-potential coulometry of two representative samples, viz. RuCl$_2$(HL^2)(L^2) and RuCl$_2$(HL^4)(L^4), at 0.0 V gave coulomb counts corresponding to one-electron transfer. The observed cyclic voltammograms thus arise from the couple in eq 1. In **3** the oxidation state of ruthenium is +2. The nearly

$$RuX_2(HL)(L) + e^- \rightleftharpoons RuX_2(HL)(L)^-$$ (1)
$$\quad\quad\quad\;\; \textbf{2} \quad\quad\quad\quad\quad\quad \textbf{3}$$
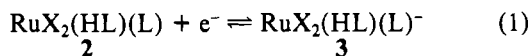
Nerstian behavior is a good indication that the gross stereochemistries of **2** and **3** are alike. The average of cathodic and anodic peak potentials were equated to the electrode potential $E°_{298}$ for the couple in eq 1. These potentials along with ΔE_p are collected in Table III. With $v \geq 100$ mV s^{-1}, ΔE_p increases, but very slowly. Some data in the range 200–400 mV s^{-1} are in Table III. The increase in ΔE_p did not affect $E°_{298}$ to any measurable extent. Green solutions of **3** produced by coulometric reduction (0.0 V) of **2** are reasonably stable particularly for the chloro complexes and can be quantitatively reoxidized to **2** by coulometry (0.75 V). The bromo complexes are less stable. An attempt to isolate salts of **3** in the crystalline state is currently in progress. Excessive solubility has hindered progress. The species **3** is considered further in a latter section of the paper.

Cyclic voltammograms were also run in dichloromethane (Table III). The reversibility quality is poorer in this solvent compared to acetonitrile as is generally the case.[1] The $E°_{298}$ values in dichloromethane are systematically less positive than those in acetonitrile. The dielectric constant of acetonitrile (36.0) is considerably higher than that of dichloromethane (8.9), and consequently Born solvation occurs better in the former. The value of $E°_{298}$ is dictated by the difference of solvation free energies between ruthenium(III) and ruthenium(II) species. This difference will be positive if the ruthenium(II) complex is better solvated (due to the presence of negative charge) than the ruthenium(III) complex (no charge). On increasing the dielectric constant of the medium, this difference becomes even more positive, thus shifting $E°_{298}$ to higher positive values.

In general the bromo complexes are reduced more readily (i.e., at higher positive potentials) than the corresponding chloro complexes. Electronic spectral data indicate (vide supra) that the t$_{2g}$ level stability increases as Br > Cl. Since in the reduction process an electron is added to the t$_{2g}$ level, the more facile reduction of the bromo complex is understandable. A similar trend is observed in the case of the
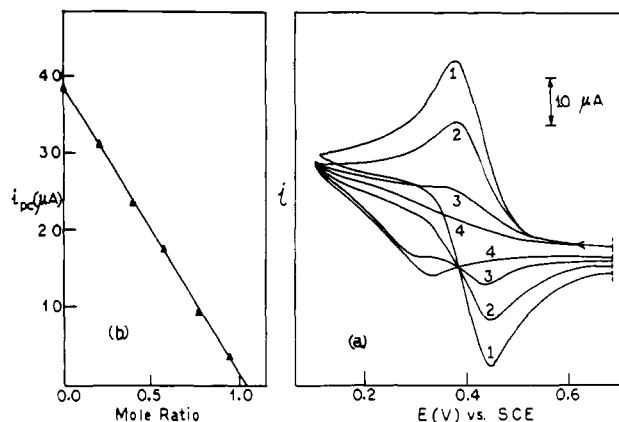

Figure 4. Effect of deprotonation on voltammetric response of RuCl$_2$(HL^1)(L^1) in CH$_3$CN: (a) cyclics at different NEt$_3$:complex mole ratios of (1) 0.04, (2) 0.39, (3) 0.76, and (4) 0.93; (b) linear plot of cathodic peak current with NEt$_3$:complex mole ratio.

α-benzil oxime complex[1] of ruthenium(III). For a given X but varying HL, $E°_{298}$ follows the order HL^1 < HL^3 ≈ HL^4 < HL^2. Clearly presence of an electron-donating group makes reduction more difficult as is expected on the basis of polar effects.[29] The electrochemical response of the present complexes were also studied with use of phase-sensitive ac voltammetry. The results to be reported elsewhere are entirely in agreement with cyclic voltammetric data. The ruthenium-(III)–ruthenium(II) $E°_{298}$ values of the present complexes can be compared with those of other chelates having the trans Ru^{III}X$_2$ moiety bound to unsaturated ligands (results on some cis-RuX$_2$ species are also given for comparison). *trans*-RuX$_2$(HB)(B) in CH$_3$CN: X = Cl, 0.46 V; X = Br, 0.50 V.[1] *trans*-RuX$_2$(pap)$_2^+$ in CH$_3$CN: X = Cl, 0.93 V; X = Br, 0.95 V.[3] *trans*-RuX$_2$(tap)$_2^+$ in CH$_3$CN: X = Cl, 0.91 V; X = Br, 0.90 V.[3] *cis*-RuX$_2$(pap)$_2^+$ in CH$_3$CN: X = Cl, 1.08 V; X = Br, 1.0 V.[3] *cis*-RuCl$_2$(bpy)$_2^+$ in CH$_2$Cl$_2$, 0.30 V[30] (pap = 2-phenylazopyridine, tap = 2-*p*-tolylazopyridine). Considering the ruthenium(III) oxidation state, the species **2** are nearly as oxidizing as *trans*-RuX$_2$(HB)(B)[1]; the cis bipyridyl complex is somewhat less oxidizing as *trans*-RuX$_2$(HB)(B);[1] the cis bipyridyl complex is somewhat less oxidizing while both trans and cis arylazopyridine species are much more oxidizing. The π-bonding interaction from metal to unsaturated ligand will be increased in the cis complexes compared to that in the trans complexes, and this fact is reflected in the redox potentials of, e.g., RuX$_2$(pap)$_2^+$.

The diffusion coefficients (*D*) of RuCl$_2$(HL)(L) were determined chronoamperometrically[31] both in acetonitrile and in dichloromethane (Table III). The coefficients are systematically smaller in the later solvent. In a given solvent diffusion becomes slower with increasing bulk in the order HL^1 > HL^2 > HL^3 > HL^4.

(b) Deprotonation and Its Effect on Electrochemical Response. Addition of base (NEt$_3$) to solutions of **2** in acetonitrile leads to progressive dimination of the electrochemical response due to the ruthenium(III)–ruthenium(II) couple near 0.45 V. When the **2**:NEt$_3$ mole ratio reaches (1:1), the cathodic current response becomes virtually zero. The case of RuCl$_2$(HL^1)(L^1) is displayed in Figure 4. The other complexes behave in exactly the same manner. On subsequent addition of HClO$_4$, the original voltammogram is reestablished (NEt$_3$:HClO$_4$ = 1:1). Evidently **2** can be deprotonated by base; reprotonation occurs on addition of acid (eq 2). The color of **4** is red. The

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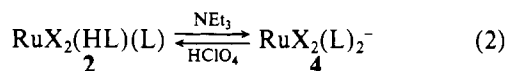(27) Sadler, J. L.; Bard, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 1979.
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$$RuX_2(HL)(L) \underset{HClO_4}{\overset{NEt_3}{\rightleftharpoons}} RuX_2(L)_2^- \qquad (2)$$
$$\mathbf{2} \qquad\qquad \mathbf{4}$$

species **4** does have a voltammetric response on the negative side (showing that ruthenium(III) is more stable in **4** than in **2**) of that of **2** (Figure 4), but the cathodic peak is very flat, and the corresponding anodic response is relatively weak. The detailed nature of the process involved has not been investigated.

The electronic spectrum of **4** was determined in acetonitrile in a few cases (Figure 2, Table II). The ~1000-nm LMCT band characteristic of **2** shifts slightly to lower energy on deprotonation. On the other hand the ~570-nm band shifts to higher energy. Addition of perchloric acid to **3** brings back the original spectrum of **2**. These experiments clearly establish the presence of a proton in **2**. The facile protonation–deprotonation reaction (eq 2) is a characteristic feature of these hydrogen–bonded complexes. The $RuX_2(HB)(B)$ complexes behave similarly. Attempts to isolate **4** in the form of salts is currently in progress.

(c) Chemical Reduction of 2 and Further Characterization of 3. The conversion **2** → **3** (eq 1) can be brought about in acetonitrile by chemical reducing agents like hydroquinone and hydrazine. Hydroquinone (H_2q) was found to be a particularly convenient reducing agent for rapid and quantitative conversion of **2** to **3**. Excess of hydroquinone is required to complete the reduction, suggesting the presence of an equilibrium process (eq 3). Perchloric acid pushes equilibrium

$$2RuX_2(HL)(L) + H_2q \rightleftharpoons 2RuX_2(HL)(L)^- + q + 2H^+$$
$$\mathbf{2} \qquad\qquad\qquad \mathbf{3}$$
$$(3)$$
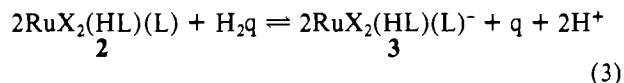
3 to the left. On addition of excess acid, H_2q no longer reduces **2**, but q is found to oxidize **3** to **2**.

Solutions of **3** are green, and both the electrochemically and chemically produced species have identical spectra (Figure 2, Table II). These spectra are quite different from those of the ruthenium(III) analogue (**2**). These are characterized by an intense band near 680 nm with a slight shoulder at ~500 nm. This band is believed to be due to metal (t_{2g}) → ligand (π^*) charge-transfer (MLCT) transition. MLCT transition is of common occurrence in ruthenium(II) complexes of conjugated ligands.[32,33] However, the band position in the present complexes is unusually low in energy. The MLCT band shifts to higher energy in the order Br > Cl. This order is opposite to that of the LMCT band of **2** (vide supra) as expected.

E. Other Complexes. We have attempted to prepare the iodo species $RuI_2(HL)(L)$ following a method similar to (NaI used instead of LiBr) that used for making the bromo complexes. Iodine-containing species thus obtained do not appear to be pure complexes, and full characterization is awaited. Some of the products show a strong EPR signal at 2.00 suggesting the presence of some free radicals. However, cyclic voltammetric data of the products in acetonitrile does show that the species $RuI_2(HL)(L)$ is most probably present to measurable extents. $E°_{298}$ values for couple 1 are as follows: HL^1, 0.55 V; HL^3, 0.50 V; HL^4, 0.53 V. The results are consistent with the expected (vide supra) order of $E°_{298}$ I > Br > Cl in **2**. Previously we have briefly reported diamagnetic pink ruthenium(II) complexes of the type $RuX_2(HL)_2$ prepared in absolute ethanol under nitrogen. These were given a tentative *trans*-$RuCl_2$ structure since a strong ν_{RuCl} was observed. We have now found that this stretch is actually due to contamination by the ruthenium(III) species $RuX_2(HL)(L)$. $RuX_2(HL)_2$ probably has a *cis*-RuX_2 structure. The system is under investigation. Arylazo oxime smoothly displaces halogen from *cis*-$Ru(bpy)_2Cl_2$ producing $Ru(bpy)_2(L)^+$ which can be readily protonated to $Ru(bpy)_2(HL)_2^+$. Further reports on such a system will be made in due course.

Registry No. $RuCl_2(HL^1)(L^1)$, 78128-51-5; $RuCl_2(HL^1)(L^1)^-$, 78128-52-6; $RuBr_2(HL^1)(L^1)$, 78128-53-7; $RuBr_2(HL^1)(L^1)^-$, 78128-54-8; $RuCl_2(HL^2)(L^2)$, 78149-26-5; $RuCl_2(HL^2)(L^2)^-$, 78128-55-9; $RuBr_2(HL^2)(L^2)$, 78128-56-0; $RuBr_2(HL^2)(L^2)^-$, 78149-27-6; $RuCl_2(L^2)_2^-$, 78128-57-1; $RuCl_2(HL^3)(L^3)$, 78128-58-2; $RuCl_2(HL^3)(L^3)^-$, 78128-59-3; $RuBr_2(HL^3)(L^3)$, 78149-19-6; $RuBr_2(HL^3)(L^3)^-$, 78149-20-9; $RuCl_2(HL^4)(L^4)$, 78128-60-6; $RuCl_2(HL^4)(L^4)^-$, 78128-61-7; $RuBr_2(HL^4)(L^4)$, 78128-62-8; $RuBr_2(HL^4)(L_4)^-$, 78128-63-9.

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Kinetics of Acid-Catalyzed Chelate Ring Opening in Nickel(II) Polyamine Complexes

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The rates of dissociation of $Ni(en)^{2+}$ and $Ni(en)_3^{2+}$ increase linearly with acid concentration at pH values below 1.5. The H_3O^+ rate constants are 0.056 and 19 M^{-1} s^{-1} (25 °C), respectively. In addition, general-acid catalysis of the $Ni(en)^{2+}$ dissociation by acetic and mono-, di-, and trichloroacetic acids occurs. Contrary to the usual behavior of general acids, the rate constants for these acids decrease as the acid strength increases: CH_3COOH, 0.30 M^{-1} s^{-1}; $ClCH_2COOH$, 0.141 M^{-1} s^{-1}; $Cl_2CHCOOH$, 0.08 M^{-1} s^{-1}; Cl_3CCOOH, 0.10 M^{-1} s^{-1}. The dissociation of $Ni(en)_3^{2+}$ exhibits no general-acid catalysis under the same conditions. A slight acceleration of the dissociation of $NiNH_3^{2+}$ occurs with H_3O^+ and acetic acid at high concentrations, but this increase is small relative to the uncatalyzed aqueous dissociation rate. These results indicate that the dissociation of chelate complexes is accelerated by protonation of the donor while it is still within the first coordination sphere. Acid attack occurs prior to or during solvent separation of the metal and amine donor. The unusual general-acid effect for $Ni(en)^{2+}$ reflects the ability of the carboxylic acids to associate with the metal complex and to transfer a proton to a donor that is in the first coordination sphere.

Introduction

Chelate dissociation is much slower than the analogous reaction of monodentate ligand complexes. However, acid can accelerate the dissociation by several orders of magnitude.

After one donor is replaced by a solvent molecule, acid assists the dissociation of a polyamine chelate complex by protonating the partially coordinated intermediate and stabilizing it relative to the fully coordinated form.[1] Thus, the ring-opening step