Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Affinity of Tetraammineruthenium(II) and -(III) for Some Amino Acid Esters

NAPAPON S. SCOTT and HENRY TAUBE*

Received February 5, 1981

As is the case with aquopentaammineruthenium(II), the affinity of *trans*-aquotetraammine(sulfito)ruthenium(II) for nitrogen donor ligands decreases on alkylation of the donor atom. The association quotients at 25 °C and μ = 0.1 M for the sulfito complex with ammonia, methylamine, ethyl glycinate, methyl sarcosinate, and the prolinato anion are 1.5×10^3, 5.4×10^2, 4.7×10^2, 3.1, and 5, respectively. The specific rates (mol^{-1} s^{-1}) for complex formation with the same ligands are 13.8, 1.9, 20, 2.9 and 5.3. The trans-sulfito group in replacing NH_3 lowers the affinity by a factor of about 10 and increases the rate of substitution by a factor of about 100. With a sulfur donor ligand, methionine methyl ester, the affinity is decreased by a much larger factor, consonant with the idea that the sulfur acts as a π acid.

Introduction

Recently, results on the affinities of aquopentaammineruthenium(II) for primary and secondary amines and the rates of substitution were presented.[1] It is apparent from these studies that the affinity of saturated nitrogen ligands for Ru(II) decreases markedly when H is replaced by alkyl groups. With tetraammine(sulfito)ruthenium(II), the trans position is quite labile[2] and equilibrium attachment of ligands is readily achieved; moreover, the equilibrium can be frozen by oxidation, thus making it possible to combine the advantages of substitution inert ligation with equilibrium control of product composition.[3] For this reason it seemed worthwile to extend the studies of affinities and rates to the tetraammine(sulfito)ruthenium(II) complex, and to include studies on R'SR and R'SH, as ligands which have biological significance.

Experimental Section

Materials. Isonicotinamide (Aldrich) was purified by recrystallizing it at least twice from hot water. Glycine ethyl ester hydrochloride (Aldrich) and sarcosine methyl ester hydrochloride (United States Biochemical) were used as received. L-Proline (Aldrich) was purified by recrystallization once from hot water. L-Methionine methyl ester hydrochloride (Aldrich) and L-cysteine ethyl ester hydrochloride (Aldrich) were also used as received. All other chemicals were of reagent grade and were used without further purification. All buffer solutions were made up with water distilled from alkaline permanganate.

trans-$[Ru(NH_3)_4SO_2Cl]Cl$ was prepared from $[Ru(NH_3)_5Cl]Cl_2$ according to Isied's procedure.[4] Elemental analyses were performed by the Stanford University Microanalytical Laboratory. Anal. Calcd for *trans*-$[Ru(NH_3)_4SO_2Cl]Cl$: Ru, 33.2; N, 18.4; H, 3.9; S, 10.5; Cl, 23.4. Found: Ru, 33.0; N, 18.3; H, 3.9; S, 10.5; Cl, 23.6. *trans*-$[Ru(NH_3)_4SO_2Cl]^+$ aquates rapidly on dissolution to yield the trans aquo complex.[3]

Electrochemical Measurements. Cyclic voltammograms were obtained with a Princeton Applied Research Model 173 potentiostat and Model 175 Universal Programmer instruments and a Houston and Instrument XY recorder. The electrochemical cell was a conventional two-compartment cell in which the saturated calomel reference electrode was isolated from the test solution by means of a glass frit. Carbon paste, platinum, and saturated calomel were used as working, counter, and reference electrodes, respectively. All measurements were performed at room temperature (25 ± 0.5 °C).

Rate Measurements. The rates of substitution were measured under pseudo-first-order conditions in buffered solutions. The rates of substitution of methionine methyl ester and cysteine ethyl ester into tetraammine(sulfito)ruthenium(II) were followed by monitoring the change in absorbance at 325 nm on a stopped-flow apparatus consisting of a thermostated Aminco-Morrow flow system adapted to fit on a Beckman DU spectrophotometer[5] and, as well, by the competition method using isonicotinamide.[6]

The rates of substitution with methylamine, glycine ethyl ester, sarcosine methyl ester, and L-proline were measured only by the competition method[6] again using isonicotinamide and by monitoring the formation of *trans*-$[Ru(NH_3)_4SO_3isn]$ at 410 nm as a function of time on a Beckman Acta MVII recording spectrophotometer.

The rates of aquation were measured by trapping the aquo complex as *trans*-$[Ru(NH_3)_4SO_3isn]$. Solutions of *trans*-$[Ru(NH_3)_4SO_3L]$ where L represents the amino acid were prepared in situ in 0.01 M of L and 1×10^{-5} M of *trans*-$[Ru(NH_3)_4SO_3H_2O]$ solution. After the reaction of *trans*-$[Ru(NH_3)_4SO_3H_2O]$ with L was complete, the solution was anaerobically transferred by syringe into buffered solutions containing isonicotinamide which had previously been degassed. After 30 s allowed for mixing, the solutions were transferred into cuvettes, and the formation of *trans*-$[Ru(NH_3)_4SO_3isn]$ was followed at 410 nm. All reactions were measured at 25 ± 0.5 °C.

Results

Substitution in *trans*-$[Ru^{II}(NH_3)_4(SO_3)H_2O]$. The visible absorption spectra of the *trans*-$[Ru(NH_3)_4(SO_3)L]$ complexes are very similar to that of the starting ruthenium complex, *trans*-$[Ru(NH_3)_4(SO_3)H_2O]$ for L = methylamine, glycinate, sarcosinate, L-proline, methionate, and cysteinate. Among the six complexes produced by substitution, *trans*-$[Ru(NH_3)_4(SO_3)NH_2CH_2CO_2C_2H_5]$ exhibited the greatest contrast in absorbance. This occurred at 325 nm, but even in this case $\Delta\epsilon$ amounts to only 82.9 M^{-1} cm^{-1} (Figure 1). Therefore, in most cases the competition method as described was adopted in determining the reaction rates. The concentration of isonicotinamide was kept in the range $(0.8–2) \times 10^{-3}$ M. All the results on the forward reaction are summarized in Table I, in which are recorded pseudo-first-order rate constants (k_{obsd}) for reactions of *trans*-$[Ru(NH_3)_4SO_3H_2O]$ with different entering ligands. The second-order rate constants for the formation,[6] k_1, can be obtained from the slope of the one-parameter least-squares fit of the plot of k_{obsd} vs. [L], and they are summarized in Table II. In the substitution reactions studied, the value of 18.2 ± 1.2 M^{-1} s^{-1} (HCO_3^-–CO_3^{2-}, pH 10, μ = 0.1 M) was found for the rate constant governing formation of *trans*-$[Ru(NH_3)_4SO_3isn]$, compared to 24 M^{-1} s^{-1} (0.1 M $NaHCO_3$, pH 8.35) previously reported.[3] The conditions are sufficiently different so that the difference in rate can be real.

Aquation of *trans*-$[Ru(NH_3)_4SO_3L]$. The rates of aquation of *trans*-$[Ru(NH_3)_4SO_3L]$ were studied independently by scavenging *trans*-$[Ru(NH_3)_4SO_3H_2O]$ as it is formed, with use of isonicotinamide. The rates were found to be independent of the isonicotinamide concentration (0.045–0.090 M) which was always at least 50 times greater than the concentration of free L. The averaged values for two different concentrations

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0020-1669/81/1320-3135$01.25/0

Table I. Substitution Reactions of *trans*-$[Ru^{II}(NH_3)_4SO_3H_2O]$ with Amino Acid Esters

L	10^3[isn], M	10^3[L], M	10^2k_{obsd}, s^{-1}	conditions
NH_3	2.46	1.95	9.0	0.1 M NH_4Cl, pH 7.8
	2.46	6.82	14.3	0.1 M NH_4Cl, pH 8.3
NH_2CH_3	1.32	4.55	2.7	HCO_3^-–CO_3^{2-}, pH 10, μ = 0.1 M
	1.32	9.10	3.2	
	1.32	13.60	3.6	
$NH_2CH_2CO_2C_2H_5$	12.50	10.00	40	Tris, pH 8
	12.50	12.50	44	μ = 0.1 M
	12.50	15.00	50	
	12.50	17.50	54	
		50.10	101	
		75.00	154	
$NH(CH_3)CH_2CO_2CH_3$	10.00	2.50	18.6	HCO_3^-–CO_3^{2-}, pH 10, μ = 0.1 M
	10.00	5.00	19.7	
	10.00	10.00	20.8	
$NH(CH_2)_3CHCOO^-$	1.71	0.299	3.5	HCO_3^-–CO_3^{2-}, pH 9.5, μ = 0.1 M
	1.71	0.599	3.7	
	1.71	1.19	4.0	
$S(CH_3)(CH_2)_2CH(NH_2)CO_2CH_3$	0.82	0.45	1.28	OAc^-, pH 5.7, μ = 0.1 M
	0.82	0.90	1.62	
	0.82	1.50	1.85	
		149	102	OAc^-, pH 5.4, μ = 0.1 M
		125	92	
		99.7	82	
		76.6	51	OAc^-, pH 3.8, μ = 0.1 M
		134	45	
		183	41	
$SHCH_2CH(NH_2)CO_2C_2H_5$	1.38	0.761	2.16	OAc^-, pH 5.7, μ = 0.1 M
	1.38	1.52	2.36	
	1.38	2.28	2.53	
		43.3	71	OAc^-, pH 3.8, μ = 0.1 M
		51.7	72	

Table II. Second-Order Rate Constants for the Formation of *trans*-$[Ru^{II}(NH_3)_4SO_3L]$ and Their Corresponding Rates of Aquation

L	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}	conditions
NH_3	13.8 ± 0.5	$(9.5 \pm 0.3) \times 10^{-3}$	0.1 M NH_4Cl
NH_2CH_3	1.9 ± 0.3[a]	$(3.5 \pm 0.1) \times 10^{-3}$	HCO_3^-–CO_3^{2-}, pH 10, μ = 0.1 M
$NH_2CH_2CO_2C_2H_5$	19.8 ± 0.3[a]	$(4.2 \pm 0.1) \times 10^{-2}$ [a]	Tris, pH 8, μ = 0.1 M
	21.2 ± 0.4[b]	$(5.4 \pm 0.4) \times 10^{-2}$ [b]	
$NH(CH_3)CH_2CO_2CH_3$	2.9 ± 0.5[a]	$(9.3 \pm 0.5) \times 10^{-1}$	HCO_3^-–CO_3^{2-}, pH 10, μ = 0.1 M
$NH(CH_2)_3CHCOO^-$ [d]	5.3 ± 0.5[a]	1.1 ± 0.5	HCO_3^-–CO_3^{2-}, pH 9.5, μ = 0.1 M
$S(CH_3)(CH_2)_2CH(NH_2)CO_2CH_3$ [c]	5.1 ± 0.3[a]	$(6.9 \pm 0.5) \times 10^{-1}$	OAc^-, pH 5.7, μ = 0.1 M
	4.9 ± 0.1[b]	$(5.5 \pm 0.2) \times 10^{-1}$	OAc^-, pH 5.4, μ = 0.1 M
	$(9.5 \pm 0.5) \times 10^{-1}$	$(5.8 \pm 0.5) \times 10^{-1}$	OAc^-, pH 3.8, μ = 0.1 M
$SHCH_2CH(NH_2)CO_2C_2H_5$	2.39 ± 0.3[a]	$(1.35 \pm 0.3) \times 10^{-1}$	OAc^-, pH 5.7, μ = 0.1 M
	1.1 ± 0.1	$(6.6 \pm 0.1) \times 10^{-1}$	OAc^-, pH 3.8, μ = 0.1 M

[a] With competitor ligand. [b] Without competitor ligand. [c] Nitrogen is protonated at prevailing pH. [d] In common with the ligands for which the site of ligation can be assigned to saturated nitrogen, the prolinato complex has an absorption maximum at 255 nm.

of isonicotinamide are given in Table II. Kinetics of the aquation reaction were studied by direct mixing of aquo(sulfito)tetraammineruthenium(II) and the appropriate ligand in buffer solution. After complex formation was allowed to proceed for ca. 1 h, 1 mL of the solution was transferred into a deaerated solution of isonicotinamide of known concentration. The extent of reaction was then monitored at λ = 410 nm.

For the substitution reactions studied by the direct method, leading to incomplete formation of the complex,[2] aquation rates were calculated from intercept of plots of k_{obsd} vs. [L].

Reduction Potentials of *trans*-$[Ru(NH_3)_4SO_3L]^{+/0}$ Couples. The Ru(II)/Ru(III) redox couples were electrochemically reversible except for L = cysteinate. The values of $E_{1/2}$ determined by cycle voltammetry are recorded in Table III.

Discussion

At a pH of 6.0 or above, S(IV) is coordinated to Ru(II) as SO_3^{2-} and to Ru(III) in this form over the whole range we have covered. Although all the ligands have more than one kind of site for ligation, there is no ambiguity on this score in any

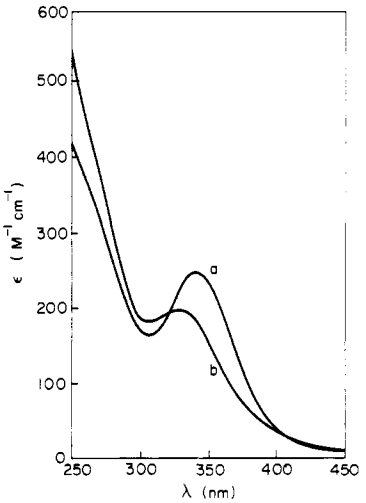

Figure 1. Absorption spectra for (a) *trans*-$[Ru(NH_3)_4SO_3H_2O]$ and (b) *trans*-$[Ru(NH_3)_4SO_3NH_2CH_2CO_2C_2H_5]$ in Tris–HCl buffer (pH 8, μ = 0.1 M, [Ru] = 1.08×10^{-3} M).

Table III. Equilibrium Data for the Tetraammine Sulfito and Pentaammine Systems[a]

	trans-$Ru(NH_3)_4SO_3H_2O$			$Ru(NH_3)_5H_2O$		
	K_{2s}[b]	K_{3s}[b,c]	$E_{1/2}$[j]	K_{2a}[b]	K_{3a}[b]	$E_{1/2}$
NH_3	1.5×10^3	1.5×10^3 [c]	0.310	$(3.5 \pm 1.3) \times 10^4$ [d,o]	7×10^4 [e]	0.050[q] (μ = 0.2 M)
NH_2CH_3	5.4×10^2	2.0×10^2	0.334	3.5×10^3 [p]	3.5×10^3 [p]	0.0[p]
$NH_2CH_2CO_2C_2H_5$	4.7×10^2	52	0.365	3.2×10^3 [p]	5.5×10^2 [p]	0.145[p]
$NH(CH_3)CH_2CO_2CH_3$	3.1	0.9	0.340	50 ± 10[p]	2.0[p]	0.185[p]
$NH(CH_2)_3CHCO_2^-$	5	3	0.323			
$S(CH_3)(CH_2)_2CH(NH_3^+)CO_2CH_3$	7.4[f]	7×10^{-3} [f]	0.486[f]	$\geq 10^5$ (5)[g]	$\geq 1 \times 10^{-2}$ (5)[g,n]	
imidazole	1.2×10^4 [k]	4.3×10^3 [k]	0.337[k]	2.8×10^6 [o]	3×10^4 [h]	0.17[o] (μ = 1.0 M)
isonicotinamide	3.8×10^3 [m]	9[k]	0.46[k]	2×10^9 [i]	1×10^4	0.375[q]

[a] At 25 °C and μ = 0.1 M. [b] K_{2s} and K_{3s} are the association quotients for the Ru(II) and Ru(III) sulfito species and K_{2a} and K_{3a} for the Ru(II) and Ru(III) pentaammine species. [c] In calculating the entries for K_{3s}, $E_{1/2}$ = 0.309 at μ = 0.10 M was used.[2] [d] Corrected for statistical factor so as to make it commensurate with the values for the sulfito system. [e] This value is a factor of 5 lower than that reported in ref 6. It is preferred because it is based on a value of E obtained under the same conditions as that for the comparison $Ru(NH_3)_5H_2O^{3+/2+}$ couple (0.067 V).[7] It should be noted that, for neutral ligands, the association quotients will not be very sensitive to μ, but E is sensitive to μ. [f] At pH 5.7 where the measurements were made, only 82% of the aquoruthenium(II) species is present as the sulfite; the balance is present as the bisulfito. The data have been corrected for this. [g] Based on $(CH_3)_2S$. [h] Because μ for the couples compared is so different, the value may be in error by as much as a factor of 10. [i] Estimated from ΔH for complex formation as determined by K. Breslauer and S. Isied (personal communication). [j] Potentials are vs. NHE and are taken as the average of anodic and cathodic peak potentials at scan rates of 100–200 mV s^{-1}. [k] Reference 2. [m] Reference 3. [n] Reference 5. [o] Reference 6. [p] Reference 1. [q] Reference 7.

of the systems. At low pH, the potential nitrogen sites are protonated, and thus Ru(II) will become attached to sulfur rather than nitrogen. An ester group is in no case a contender for stable attachment to Ru(II), and though complications can ensue from N to ester isomerization for Ru(III) at low pH,[9] this has not been a factor in our work, where Ru(III) has been featured only on a very short time scale, that of a cyclic voltammetry trace.

Summarized in Table III are the equilibrium data accumulated in this study, as well as related data which make it possible to assess the effect on the affinity of replacing an ammonia trans to the entering ligand with SO_3^{2-}. Such data are of use in trying to understand the qualities of SO_3^{2-} in its interaction with a metal ion. The comparisons possible in the ruthenium system are particularly useful because the response of Ru(II), which readily lends itself to back-bonding interactions, can be compared to that of Ru(III), for which back-bonding is much less prominent.

In comparing the entries K_{2s} and K_{2a} in Table III for Ru(II), it is apparent that, while a sulfito group replacing NH_3 in the trans position causes a decrease in affinity in every case, this decrease is a factor of only about 20 for a saturated ligand such as NH_3, but it approaches 10^6 for an unsaturated one like isonicotinamide. This suggests that SO_3^{2-} does act as a π acid in spite of carrying a 2– charge. In all likelihood, the so-called synergism between σ and π components of the Ru–S bond are important in a case like this. A large decrease is registered also for a thio ether, in keeping with the idea that back-bonding is important for the Ru(II)–SR_2 interaction, and a smaller decrease for imidazole, which appears to be only a weak π acid. The comparison between the methionine methyl ester and dimethyl sulfide is complicated because at the pH of the measurements;[10] the former is protonated (pK 7.1),[10] but because the positive charge is four atoms removed, the effect on the affinity is probably less than a factor of 10.

We had hoped to provide a comparison between HS–R and R′–S–R as ligands, but our hopes were frustrated because, at a pH high enough to provide the sulfito complex as reactant, proton dissociation from the thiol takes place. At pH 3.8, the dominant form of Ru(II) in solution is $[Ru(NH_3)_4(HSO_3)H_2O]^+$, but now the affinity of the ligands for Ru(II) is so low that the equilibrium data are undependable (at a pH of 3.8, where $[Ru(NH_3)_4(HSO_3)H_2O]^+$ is the dominant form, K_{2s} for the methionate was determined as 1.6).

As to the values obtained for Ru(III), invariably K_{3s} is less than K_{3a}, but the excursion range for the K_{3s}/K_{3a} ratios is smaller than for K_{2s}/K_{2a}. This difference is attributable to the extra component in the bonding in the Ru(II) case, back-bonding being very sensitive to the nature of the auxiliary ligands.

We turn now to a consideration of the kinetic data. It should be noted that, where measurements were made both by the direct reaction and by the competition method, there is good agreement. As a result, we are confident that isonicotinamide in the reaction solution does not cause unanticipated complications. The competition method is preferred owing to its sensitivity. The rate constants for substitution span a range of 2–20 M^{-1} s^{-1}, somewhat larger than is the case for $[Ru(NH_3)_5H_2O]^{2+}$. The increased sensitivity of the rate to the nature of the entering group for the sulfito case indicates that there is somewhat more bond making in the activated complex, which is in line with SO_3^{2-} being in net somewhat electron withdrawing.

The substitution rates of amino acid esters where nitrogen is the site of coordination are 10–100 fold greater than those for aquopentaammineruthenium(II).[1] The observed rates decrease as the entering ligand is changed from primary to secondary amines suggesting that, as has been observed for $[Ru(NH_3)_5H_2O]^{2+}$, a steric effect is significant in these substitution reactions. Moreover, comparison of k_1 for L = NH_2CH_3 and $NH_2CH_2CO_2C_2H_5$ shows that the polar group somewhat enhances the rate.

Because thioethers in water are weak nucleophiles toward protons, the studies with these ligands could be carried to lower pH. Of the two ligands studied, only the data for the methionine ester are readily interpretable. When allowance is made for the proportion of the Ru(II) aquo complex present as $[Ru(NH_3)_4(HSO_3)H_2O]^{2+}$ (18%) at pH 5.7, the specific rate for substitution of the methyl ester or $[Ru(NH_3)_4(SO_3)H_2O]$ is calculated as 5.7 M^{-1} s^{-1}. At pH 3.8, $[Ru(NH_3)_4HSO_3(H_2O)]^+$ is the dominant form and the specific rate for substitution is less (ca. 1 M^{-1} s^{-1}) as expected because HSO_3^- is a stronger π acid than SO_3^{2-}. At pH low enough so that $[Ru(NH_3)_4(SO_2)H_2O]^{2+}$ is the dominant form,[3] the affinity of the thioether is so low that no reaction was observed at the ligand concentration we used.

Acknowledgment. Support of this work by National Institutes of Health Grant No. GM13638-15 is gratefully acknowledged.

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Registry No. *trans*-$[Ru^{II}(NH_3)_4SO_3H_2O]$, 51175-04-3; *trans*-$[Ru^{II}(NH_3)_4SO_3H_2O]^+$, 78198-94-4; NH_3, 7664-41-7; NH_2CH_3, 74-89-5; $NH_2CH_2CO_2C_2H_5$, 459-73-4; $NH(CH_3)CH_2CO_2CH_3$, 5473-12-1; $\overline{NH(CH_2)_3CHCOO}^-$, 17781-82-7; $S(CH_3)(CH_2)_2CH(NH_2)CO_2CH_3$, 10332-17-9; $SHCH_2C(NH_2)HCO_2C_2H_5$, 3411-58-3; *trans*-$[Ru^{II}(NH_3)_4SO_3NH_3]$, 51174-85-7; *trans*-$[Ru^{II}(NH_3)_4SO_3NH_2CH_3]$, 78198-95-5; *trans*-$[Ru^{II}(NH_3)_4SO_3NH_2CH_2CO_2C_2H_5]$, 78198-96-6; *trans*-$[Ru^{II}(NH_3)_4SO_3NH(CH_3)CH_2CO_2CH_3]$, 78217-00-2; *trans*-$[Ru^{II}(NH_3)_4SO_3\overline{NH(CH_2)_3CHCOO}]^-$, 78198-97-7; *trans*-$[Ru^{II}(NH_3)_4SO_3S(CH_3)(CH_2)_2CH(NH_3)CO_2CH_3]^+$, 78198-98-8; *trans*-$[Ru^{II}(NH_3)_4SO_3SHCH_2C(NH_2)HCO_2C_2H_5]$, 78198-99-9; *trans*-$[Ru^{III}(NH_3)_4SO_3NH_3]^+$, 78199-00-5; *trans*-$[Ru^{II}(NH_3)_4SO_3NH_2CH_3]^+$, 78199-01-6; *trans*-$[Ru^{III}(NH_3)_4SO_3NH_2CH_2CO_2C_2H_5]^+$, 78393-32-5; *trans*-$[Ru^{III}(NH_3)_4SO_3\overline{NH(CH_3)CH_2CO_2CH_3}]^+$, 78247-42-4; *trans*-$[Ru^{III}(NH_3)_4SO_3\overline{NH(CH_2)_3CHCOO}]$, 78408-00-1; *trans*-$[Ru^{III}(NH_3)_4SO_3S(CH_3)(CH_2)_2CH(NH_3)CO_2CH_3]^{2+}$, 78393-33-6.

Contribution from the Department of Inorganic Chemistry,
Indian Association for the Cultivation of Science, Calcutta 700 032, India

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

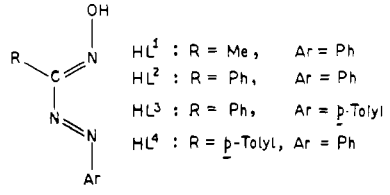
A. R. CHAKRAVARTY and A. CHAKRAVORTY*

Received January 13, 1981

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_4X_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



HL^1 : R = Me, Ar = Ph
HL^2 : R = Ph, Ar = Ph
HL^3 : R = Ph, Ar = p-Tolyl
HL^4 : R = p-Tolyl, Ar = Ph

1

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] $RuCl_3 \cdot 3H_2O$ 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_3CN was prepared by directly adding a known weight of the freshly distilled amine to the CH_3CN 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_3CN 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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