Inorg. Chem. **1980**, *19*, 865–869 **865**

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Registry No. $[Ru(bpy)_2(t\text{-}Bu(py))_2](PF_6)_2$, 72525-66-7; $[Ru(bpy)_2(py)(NO_2)](PF_6)$, 36309-80-5; $Ru(bpy)_2Cl_2$, 19542-80-4; $[Ru(bpy)_2(py)(NO_3)](PF_6)$, 72378-65-5; $[Ru(bpy)_2(py)_2](PF_6)_2$, 72525-67-8; $[Ru(bpy)_2(py)_2](NO_3)_2$, 72525-68-9; $[Ru(bpy)_2(py)(ClO_4)](ClO_4)$, 72525-70-3; $[Ru(bpy)_2(py)_2](ClO_4)_2$, 63338-39-6; $[Ru(bpy)_2(py)(p\text{-}CH_3C_6H_4SO_3)](PF_6)$, 72525-72-5; $[Ru(bpy)_2(t\text{-}Bu(py))(CF_3CO_2)](PF_6)$, 72525-74-7; $Ru(bpy)_2Cl(NCS)$, 72525-75-8; $[Ru(bpy)_2(py)(NCS)](PF_6)$, 72525-77-0; $[Ru(bpy)_2(py)(OH_2)](PF_6)_2$, 72525-78-1; $[Ru(bpy)_2(py)Cl](PF_6)$, 36413-31-7; $Ru(bpy)_2(NCS)_2$, 66238-39-9; $[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$, 55124-54-4; $Ru(bpy)_2Br_2$, 23377-85-7; $[Ru(bpy)_3](PF_6)_2$, 60804-74-2; $[Ru(bpy)_2(py)CH_3CN](PF_6)_2$, 72525-79-2; $Ru(bpy)_2(NCS)Cl$, 72525-75-8; $[Ru(bpy)_2(py)ClO_4]PF_6$, 72525-80-5; $[Ru(bpy)_2(py)CF_3CO_2]PF_6$, 72525-82-7; $[Ru(bpy)_2(t\text{-}Bu(py))H_2O](PF_6)_2$, 72525-84-9; $[Ru(bpy)_2(py)H_2O](PF_6)_2$, 72525-78-1; $[Ru(bpy)_2(t\text{-}Bu(py))NO_3]PF_6$, 72525-86-1; $[Ru(bpy)_2(py)NCS]Cl$, 72525-87-2; $[Ru(bpy)_3](SCN)_2$, 72525-88-3; $[Ru(bpy)_2(py)Br]^+$, 72558-80-6.

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Alkyl Nitrite Complexes of Ruthenium Prepared by Acid–Base Chemistry at the Bound Nitrosyl Group

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The alkyl nitrite complexes $[Ru(bpy)_2(py)N(O)OR]^{2+}$ (bpy = 2,2′-bipyridine; py = pyridine; R = methyl, ethyl, *n*-butyl, isopropyl) have been prepared by reactions involving attack of the corresponding alkoxide ions on the nitrosyl nitrogen in $[Ru(bpy)_2(py)NO]^{3+}$. In the products the alkyl nitrite groups appear to be N bound. From the properties of the complexes, it seems that $d\pi(Ru^{II}) \rightarrow \pi^*(N(O)OR)$ back-bonding is significant and that the alkyl nitrite group is a better π-electron acceptor than the nitro, pyridyl, or acetonitrile groups when bound to Ru(II). The complexes form in dry acetonitrile when both alcohol and base (collidine) are added, $Ru(bpy)_2(py)NO^{3+} + ROH + B \rightarrow Ru(bpy)_2(py)N(O)OR^{2+} + BH^+$, and the reversible nature of the chemistry is seen following the addition of excess acid, $Ru(bpy)_2(py)N(O)OR^{2+} + H^+ \rightarrow Ru(bpy)_2(py)NO^{3+} + ROH$. Once formed, the alkyl nitrite complexes undergo an irreversible, one-electron oxidation (at $\sim$+1.75 V vs. SSCE) and the major products are $[Ru(bpy)_2(py)NO]^{3+}$ and ROH. The chloro analogues $[Ru(bpy)_2(Cl)N(O)OR]^+$ (R = ethyl, isopropyl) have also been prepared, in this case by attack of RO^- on $[Ru(bpy)_2(Cl)NO]^{2+}$. It has proven difficult to characterize the complexes fully, but they appear to have properties similar to those found for the pyridyl complexes.

Introduction

Metal nitrosyl complexes with relatively high NO stretching frequencies (>1850 cm^{-1}) have a sufficiently high degree of NO^+-like ligand character that they undergo a series of reactions involving nucleophilic attack at the nitrosyl group.[1-5] The chemistry involved is often similar to reactions observed for relatively electron-deficient compounds containing the isoelectronic CO ligand.[6] Attack by OH^-, SH^-, N_3^-, and N_2H_4 has been found for metal nitrosyl complexes with appropriately high NO stretching frequencies.[2] Complexes of the type $[Ru(bpy)_2(L)NO]^{n+}$ (bpy = 2,2′-bipyridine; L = Cl^-, pyridine) ($\nu(NO) > 1930$ cm^{-1}) fit well into this reactivity pattern in that their reactions with nucleophiles such as OH^-, N_3^-, aromatic amines, and phenoxide ion have been reported.[7-11] The reactions with OH^- are of interest in the present study because oxidation of the resulting nitro complexes, e.g., $[Ru^{II}(bpy)_2(py)NO_2]^+$, to Ru(III) gives short-lived intermediates which have been reported to act as net oxygen atom donors in the catalytic oxidation of triphenylphosphine to triphenylphosphine oxide.[12,13]

Reed and Roper have reported[14] a series of acid–base reactions between alcohols and the nitrosyl complex $[IrCl_3(PPh_3)_2NO]^+$ which gave as products the complexes $IrCl_3(PPh_3)_2N(O)OR$, in which there are N-bound alkyl nitrite ligands. Similar reactivity for the ruthenium complex $[Ru(bpy)_2(py)NO]^{3+}$ was suggested by spectral changes observed when the complex was treated with alcohols under basic conditions. Isolation and characterization of the products seemed to be a worthwhile extension of the chemistry of the bound nitrosyl group. Of potentially more importance were the redox properties of the resulting complexes. As mentioned above, the analogous Ru(III) nitro complexes are known to

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Table I. Elemental Analysis Data

compd $[Ru(bpy)_2(py)N(O)OR](PF_6)_2$	compn					
	calcd, %			found, %		
	C	H	N	C	H	N
$R = CH_3$	37.02	2.87	9.96	36.36	2.30	9.58
$R = C_2H_5$	37.80	3.06	9.80	37.30	2.76	9.12
$R = n\text{-}C_4H_9$	39.33	3.41	9.49	36.27	3.02	8.54
$R = i\text{-}C_3H_7$	38.60	3.24	9.64	38.32	3.11	9.49

undergo intermolecular reactivity as oxygen atom transfer reagents (eq 1).[13] For the alkyl nitrite complexes, a potentially

$$(bpy)_2Ru^{III}(py)NO_2^{2+} + PPh_3 \rightarrow (bpy)_2Ru^{II}(py)NO^{2+} + OPPh_3 \quad (1)$$

oxidizable substrate (RO^-) is bound to the complex by attachment at a ligand, and it seemed possible that an intramolecular oxygen atom transfer might occur. One real advantage of such a reaction would be the possibility of developing a catalytic route for the selective oxidation of alcohols.

Experimental Section

The preparations of $[Ru(bpy)_2(Cl)NO](PF_6)_2$[16] and of $[Ru(bpy)_2(py)NO](PF_6)_3$[16] from $[Ru(bpy)_2(py)NO_2]PF_6$[17] have been described elsewhere. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium chloride and perchloric acid by mixing aqueous solutions of each, collecting the product by filtration, recrystallizing twice from water, and drying in a vacuum oven. Spectrograde acetonitrile (MCB) was used as solvent in most experiments, and all other materials were reagent grade and used without further purification.

Electrochemical experiments were carried out by using a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer. Cyclic voltammograms were obtained by using a platinum bead working electrode, platinum wire counterelectrode, and a saturated sodium chloride calomel (SSCE) reference electrode. The concentration of complexes used in the experiments was ~1 mM. Exhaustive electrolyses were carried out by using platinum gauze electrodes. Electrolyte solutions (0.1 M) contained TEAP in CH_3CN or $LiClO_4$ in CD_3CN.

Infrared and ultraviolet-visible spectra were obtained on Beckman IR 4250 and Bausch and Lomb Model 210 spectrometers, respectively. NMR spectra were obtained on a Varian XL-100 spectrometer in the FT mode using CD_3CN as solvent and tetramethylsilane as an internal reference. Photolyses were performed in Pyrex vessels with a GE sunlamp (275 W).

$[Ru(bpy)_2(py)N(O)OR](PF_6)_2$ (R = methyl) was prepared as follows. Potassium metal (15 mg) was added to 10 mL of methanol and allowed to dissolve. A 4-mL aliquot of this solution was added to a solution containing $[Ru(bpy)_2(py)NO](PF_6)_3$ (100 mg) in 20 mL of acetonitrile which led to an immediate deepening in the color of the acetonitrile solution. Methylene chloride (20 mL) was added and the solution was filtered under N_2 pressure. Diethyl ether (50 mL) was added, and the resulting precipitate was collected by filtration under N_2 and dried in a vacuum desiccator; yield 60 mg (80%). All other alkyl nitrite complexes (L = py; R = ethyl, *n*-butyl, isopropyl) were prepared by the same procedure. Our experience has been that it is difficult to obtain consistently reliable elemental analysis data on the isolated solids because the complexes decompose slowly both in the solid state and in solution. Elemental analysis data (Integral Microanalytical Laboratories, Raleigh, NC) are given in Table I. It should be noted that the experiments described below were carried out by using freshly prepared samples whose spectral and electrochemical properties were consistent with a high degree of purity.

Results and Discussion

Formation of Complexes. The optical spectrum of an acetonitrile solution containing $[Ru(bpy)_2(py)NO]^{3+}$ and 2-propanol is shown in Figure 1A. Addition of the proton base collidine (2,4,6-trimethylpyridine) results in the appearance of an absorption band at $\lambda_{max} = 400$ nm (Figure 1B). The band disappears on the addition of excess trifluoroacetic acid (Figure 1C). The spectral observations are consistent with the acid–base chemistry summarized in eq 2. In reaction 2

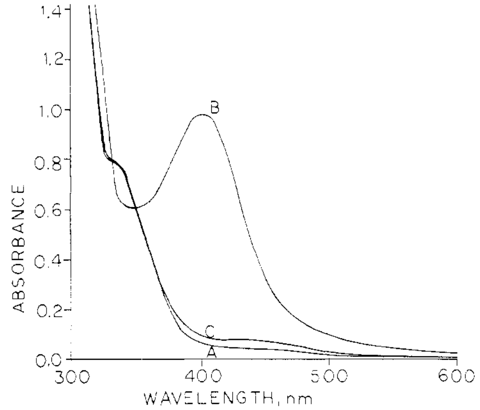
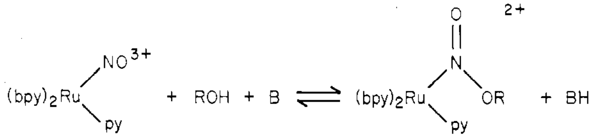
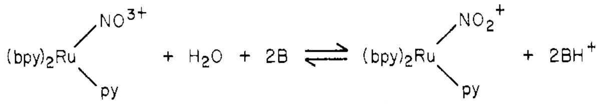


Figure 1. Formation of $[Ru(bpy)_2(py)N(O)OCH(CH_3)_2]^{2+}$ in acetonitrile solutions: (A) spectrum of $[Ru(bpy)_2(py)NO]^{3+}$ and 2-propanol (0.5 M); (B) spectrum after addition of collidine (5×10^{-4} M) to A; (C) spectrum after addition of excess trifluoroacetic acid to B.



(2)

the addition of a base, RO^- in the net sense, occurs at the nitrosyl group giving a product which contains a bound alkyl nitrite group. An entirely analogous reaction occurs in an acetonitrile solution to which water and collidine have been added, but the added base becomes O^{2-} and the product is the corresponding nitro complex[12] with $\lambda_{max} = 449$ nm[18] (eq 3).



(3)

Synthetically, it has proven advantageous to use reactions between the nitrosyl complex and the appropriate alkoxide ion in alcohol–acetonitrile solutions as a preparative route, and we have prepared the series of complexes $[Ru(bpy)_2(py)N(O)OR]^{2+}$ (R = methyl, ethyl, isopropyl, and *n*-butyl). The products presumably have the cis geometry at Ru.[19] They are unstable in the solid state as PF_6^- salts with noticeable decomposition occurring after 24–48 h in samples stored either in the atmosphere or in an evacuated desiccator. Acetonitrile solutions of the complexes are stable for at most a few hours. The decomposition products included the nitrosyl and the nitro complexes as well as other unidentified products.

Attempts to isolate the complexes where R = *tert*-butyl or benzyl were unsuccessful. Spectral studies in acetonitrile with the added alcohol (~0.5 M) and collidine (~6×10^{-4} M) showed by the absence of significant absorption at ~400 nm that, at best, the extent of nitrosyl to alkyl nitrite conversion was low. From the spectral studies, significant amounts of $[Ru(bpy)_2(py)NO_2]^+$ were formed apparently by eq 3 where the source of water must be trace amounts in the acetonitrile used. Molecular models show that formation of a *tert*-butyl

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Table II. Spectral Data for the Complexes $[Ru(bpy)_2(py)N(O)OR]^{2+}$

compd $[Ru(bpy)_2(py)N(O)OR](PF_6)_2$	visible spectral data[a] λ_{max}, nm (ϵ)	IR spectral data[b] ν, cm^{-1}	NMR spectral data[c]
$R = CH_3$	399 (10300)	~1500,[d] 972	3.83
$R = C_2H_5$	398 (9700)	~1480,[d] 940	4.30
$R = n\text{-}C_4H_9$	399 (10400)	~1500,[d] 965, 950	4.25
$R = i\text{-}C_3H_7$	399 (11400)	~1490,[d] 930	5.31

[a] Acetonitrile solution. [b] KBr pellet. [c] Chemical shift of α protons, δ vs. Me_4Si. CD_3CN solution. bpy and py proton signals are multiplets at 7–9 ppm. Other alkyl proton chemical shifts were close to those of the free alcohols. [d] Overlaps bpy ligand absorptions

nitrite complex is probably highly unfavorable because of severe steric crowding.

Spectral Studies. UV–visible spectra for the alkyl nitrite complexes in acetonitrile are characterized by intense bands ($\epsilon \approx 10^4$) at $\lambda_{max} \sim 400$ nm (Table II) which are relatively unaffected by changes in the nature of the alkyl group. From spectral assignments for closely related bis(2,2′-bipyridyl) complexes of Ru(II), the bands at 400 nm can reasonably be assigned to $d\pi(Ru) \rightarrow \pi^*(bpy)$, metal to ligand charge-transfer (MLCT) bands.[20]

Earlier work on complexes of the type *cis*-$Ru^{II}(bpy)_2L_2$ has shown that $d\pi(Ru) \rightarrow L$ back-bonding stabilizes the $d\pi(Ru)$ levels but leaves the $\pi^*(bpy)$ levels relatively unaffected.[21] As a consequence, the energies of the MLCT transitions for a related series of complexes provide a relative measure of the ability of the L group to function as a π-acceptor ligand when bound to Ru(II). By this reasoning, the alkyl nitrite ligands function as strong π-electron acceptors which are stronger than nitro, pyridyl, or acetonitrile ligands where the corresponding complexes of the type $[Ru^{II}(bpy)_2(py)L]$ have λ_{max} values at 449,[18] 455,[21] and 437 nm.[22]

Infrared spectra of the complexes as PF_6^- salts include bands consistent with the presence of N-bound alkyl nitrite ligands (Table II). In addition to the usual 2,2′-bipyridyl and pyridyl bands, partly hidden bands appear at ~1500 cm^{-1} which can be assigned to the terminal $\nu(N{=}O)$ stretching frequency, and bands also appear at ~950 cm^{-1} which is in an energy region consistent with the $\nu(O\text{–}R)$ frequency. A very similar pattern of IR bands has been reported by Reed and Roper[14] for the complexes $IrCl_3(PPh_3)_2N(O)OR$, and the assignments made here are also reasonable given the spectra of the uncoordinated ligands.[23] For the free ligand, $ONOC_2H_5$, the terminal $\nu(NO)$ bands occur at 1608 and 1650 cm^{-1} for the cis and trans isomers, respectively. The lowering in energy of the $\nu(NO)$ frequency upon coordination is consistent with considerable $d\pi(Ru) \rightarrow \pi^*(N(O)OR)$ back-bonding in the complexes. The $\nu(NO)$ frequency is considerably higher than frequencies for the $\nu(NO)$ bands for the nitro group in $[Ru(bpy)_2(py)NO_2]^+$ (1299 and 1340 cm^{-1})[10] suggesting that there is considerable localization of double bond character in the terminal NO bond as expected. Although the free ligands are known to exist as cis–trans isomers,[23] we have found no spectroscopic or chemical evidence which suggests that cis–trans isomers exist in the complexes.

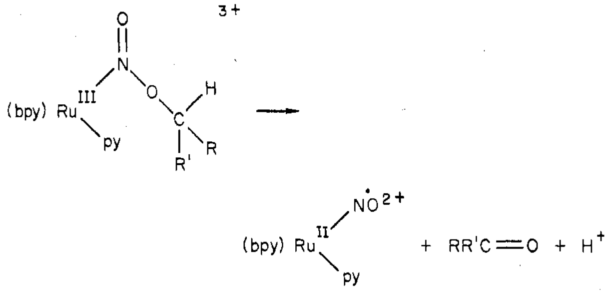
The ^1H NMR spectra of the alkyl nitrite complexes $[Ru(bpy)_2(py)N(O)OR]^{2+}$ (R = methyl, ethyl, isopropyl, *n*-butyl) consist of broad, highly coupled resonances at 7–9 ppm due to bipyridyl and pyridyl protons and resonances for the alkyl group which have the same pattern as found in the corresponding alcohols. The chemical shifts of protons at positions α to the ONO group (Table II) are found at values roughly halfway between those reported for the free alcohols and those for the free alkyl nitrites.[24] There are only small differences between the chemical shifts of the other protons in the alkyl groups and the chemical shifts of the protons in the corresponding alcohols.

Table III. Electrochemical Data in Acetonitrile Solution ($I = 0.1$ M)

compd	$E_{p,a}$,[a] V	n[b]	$[Ru(bpy)_2(py)NO]^{3+}$/ $[Ru(bpy)_2(py)CH_3CN]^{3+}$ [c]
$[Ru(bpy)_2(py)ONOR]^{2+}$			
$R = CH_3$	1.76	1.0	89/11
$R = C_2H_5$	1.75	1.0	86/14
$R = n\text{-}C_4H_9$	1.73	1.0	87/13
$R = i\text{-}C_3H_7$	1.77	1.1	87/13
$[Ru(bpy)_2(Cl)ONOR]^+$			
$R = C_2H_5$	1.24	0.9	100/0[d]
$R = i\text{-}C_3H_7$	1.23	0.8	100/0[d]

[a] $E_{p,a}$ is the peak current potential for the irreversible oxidation in CH_3CN (0.1 M $(NEt_4^+)(ClO_4^-)$) solution when scanned at 200 mV/s. [b] Number of moles of electrons removed per mole of ruthenium upon exhaustive electrolysis in acetonitrile (0.1 M $(NEt_4^+)(ClO_4^-)$) solution. [c] The product ratio was estimated from relative peak currents for the appropriate couples following exhaustive electrolysis. [d] The fractions refer to the ratio $[Ru(bpy)_2(Cl)NO]^{2+}/[Ru(bpy)_2(Cl)CH_3CN]^{2+}$

Redox Chemistry. The chemistry following oxidation of the Ru(II) alkyl nitrite complexes was the primary origin of our interest in the complexes. As mentioned in the Introduction, oxidation of $[Ru^{II}(bpy)_2(py)NO_2]^+$ to Ru(III) creates an intermolecular, oxygen-atom transfer reagent (eq 1) in which there are two, one-electron acceptor sites, one at the metal ($Ru(III) \rightarrow Ru(II)$) and one at a ligand ($RuNO^+ \rightarrow Ru\dot{N}O$).[12,13] The intent at this stage was to bind an alcohol as an alkoxide ion at the two-electron acceptor site. The point was that, with the substrate attached, it might be possible to achieve a controlled, intramolecular oxidation (eq 4). Such reactions would have the advantages of functional group specificity because of the initial binding step (eq 3) and of stereochemical selectivity given our inability to prepare alkyl nitrite complexes where R = *tert*-butyl or benzyl. There is also the possibility of inducing optical selectivity since the metal site is inherently chiral in the coordination environment of the complex.



(4)

A cyclic voltammogram of the complex $[Ru(bpy)_2(py)N(O)OC_2H_5]^{2+}$ in acetonitrile is shown in Figure 2B. On the initial oxidative sweep, a single, irreversible oxidation wave is observed at +1.75 V. Even though the wave is chemically

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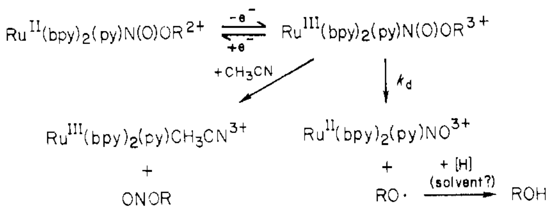
Scheme I



irreversible, the magnitude of the potential is revealing. The sizable positive shift compared, for example, with $E_{1/2} = 1.20$ V for the $Ru(bpy)_3^{3+/2+}$ couple,[25] is consistent with the conclusion reached in discussing the MLCT bands, namely, that back-bonding to $\pi^*(N(O)OR)$ leads to a considerable stabilization of $d\pi$ levels in Ru(II).[21] The potentials also mean that the Ru(III) form of the Ru(III)/Ru(II) couple is a powerful one-electron oxidizing agent (~2.0 V vs. NHE).

As shown in Figure 2B, a reverse scan following the initial oxidative sweep results in the appearance of two new, reversible waves at $E_{1/2}$ = +0.53 and +1.35 V. From known potentials,[21,22] these waves arise from the couples $Ru(bpy)_2(py)NO^{3+/2+}$ ($E_{1/2}$ = +0.53) and $Ru(bpy)_2(py)CH_3CN^{3+/2+}$ ($E_{1/2}$ = +1.35). Exhaustive electrolysis at +1.85 V gave an n value of 1.0, where n is the number of electrons removed per complex during the electrode reaction. The oxidative peak potential, the nature of the following scans, and the n value in the electrolysis experiment are all independent of the nature of the alkyl group in the –N(O)OR ligand (Table III).

Following electrolysis, the only ruthenium products in the solution were $[Ru(bpy)_2(py)NO]^{3+}$ and $[Ru(bpy)_2(py)CH_3CN]^{3+}$ with the nitrosyl complex clearly being the dominant product (Table III). To ascertain the fate of the alkyl nitrite ligand, we exhaustively electrolyzed CD_3CN (0.1 M in $LiClO_4$) solutions containing $[Ru(bpy)_2(py)N(O)OR]^{2+}$ (R = methyl, ethyl, *n*-butyl, isopropyl) at 1.85 V and obtained proton NMR spectra of the resulting solutions. The only organic products observed in significant amount were the parent alcohols. Integrated peak intensities showed that about 70% of the alkyl nitrite ligand had been converted into the alcohol.

A reasonable interpretation of the oxidation results is shown in Scheme I. In the initial step, Ru(II) is oxidized to Ru(III). Once formed, Ru(III) is a powerful one-electron-transfer oxidant. In fact, according to Scheme I, it is a sufficiently powerful oxidant that intramolecular electron transfer can occur from the –OR group to Ru(III) giving the nitrosyl complex and an alkoxy radical.

In contrast to the relatively slow scan rate used in the experiment shown in Figure 2B, at a scan rate of 10 V/s, the cyclic voltammogram of $[Ru(bpy)_2(py)N(O)OC_2H_5]^{2+}$ exhibits approximately reversible behavior for the oxidation at +1.75 V (Figure 2A).[26] Apparently at fast scan rates, the oxidized complex once formed can be recaptured at the electrode by reduction before intramolecular oxidation of the bound ligand (k_d in Scheme I) can occur. An analysis of the results of a series of cyclic voltammograms at scan rates between 0.2 and 10 V/s based on the treatment given by Nicholson and Shain[27] gave $k_d \sim 5\ s^{-1}$. The primary origin of the relatively slow rate constant for intramolecular electron transfer probably has as its origin the thermodynamic unfavorability of forming the alkoxy radical.[28] For the alcohols to be products, the alkoxy radicals once formed must undergo a hydrogen atom abstraction reaction, presumably from acetonitrile, a reaction which appears to be rapid.[29]

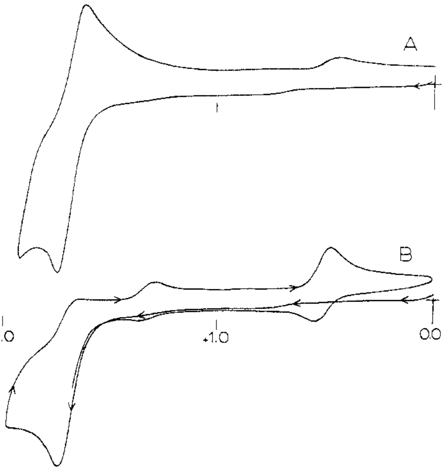


Figure 2. Cyclic voltammogram of $[Ru(bpy)_2(py)N(O)OC_2H_5]^{2+}$ (~1 mM) in acetonitrile (0.1 M $(NEt_4^+)(ClO_4^-)$): (A) scan rate = 10 V/s; (B) scan rate = 0.2 V/s.

The important point for us is that there is no evidence for the two-electron-oxidation pathway suggested in eq 4. Apparently the strength of the Ru(III) site as a one-electron oxidant is sufficient that the oxygen atom transfer step suggested by eq 4 is noncompetitive with simple one-electron transfer.

The appearance of small amounts of $[Ru^{III}(bpy)_2(py)CH_3CN]^{3+}$ in the reaction mixture can be explained by a solvolysis reaction which is competitive with electron transfer, although we have no evidence for free alkyl nitrite in the solutions following electrolysis. A facile solvolysis would be expected if an important element in the stability of the Ru^{II}–N(O)OR bond arises from Ru → $\pi^*(N(O)OR)$ back-bonding since the back-bonding interaction would be lost on oxidation to Ru(III).

Other Reactions. The alkyl nitrite complexes are photochemically active in acetonitrile solution. When exposed to light from a sunlamp (GE 275 W), spectral changes are observed which are consistent with the photosolvolysis reaction in eq 5. With time, an absorption band appears at λ_{max} =

$$Ru(bpy)_2(py)N(O)OR^{2+} + CH_3CN \xrightarrow{h\nu} Ru(bpy)_2(py)CH_3CN^{2+} + ONOR(?) \quad (5)$$

436 nm consistent with the formation of $[Ru(bpy)_2(py)CH_3CN]^{2+}$.[22] The reactions appear to be complete within a period of minutes.

We have also searched for alcohol exchange reactions based on NMR analysis of the products isolated after reactions in which either the salt $[Ru(bpy)_2(py)N(O)OCH(CH_3)_2](PF_6)_2$ was stirred in contact with an ethanol solution or the complex $[Ru(bpy)_2(py)N(O)OCH_3]^{2+}$ was dissolved in an acetonitrile–ethanol solution. In neither case was alcohol exchange observed after a period of 30 min.

$[Ru(bpy)_2(Cl)N(O)OR]^+$ Complexes. The alkyl nitrite complexes in which the cis ligand is a chloride rather than pyridine, $[Ru(bpy)_2(Cl)N(O)OR]^+$ (R = ethyl, isopropyl), were prepared by reactions between $(Ru(bpy)_2(Cl)NO]^{2+}$ in acetonitrile and alcoholic solutions containing the alkoxides. The chloro complexes are significantly less stable than the pyridyl complexes and analytically pure solids could not be obtained. However, the properties of the impure samples suggested that their behavior is similar to that of the pyridyl

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(26) The difference between anodic and cathodic peak potentials at a scan rate of 10 V/s was about 100 mV as compared to 60 mV theoretical. Given the cell configuration used, the difference is no doubt due to uncompensated cell resistance.

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complexes, and it seems relevant to discuss some of them here.

The infrared spectrum of $[Ru(bpy)_2(Cl)N(O)OC_2H_5]^{2+}$ includes bands assignable to ν(NO) and ν(O–R) modes at $\sim$1500 cm^{-1} (partially hidden by bpy ligand bands) and 930 cm^{-1}, respectively. The shift of the MLCT band to lower energy (λ_{max} = 417 nm) for $[Ru(bpy)_2(Cl)N(O)OC_2H_5]^+$ compared to the pyridyl complex is consistent with the effect of a chloro group compared to a back-bonding pyridyl ligand. The effect is also seen in the much lower potential for oxidation of Ru(II) to Ru(III) as seen by cyclic voltammetry ($E_{p,a}$ = +1.24 V). Exhaustive electrolysis of an acetonitrile solution containing $[Ru(bpy)_2(Cl)N(O)OC_2H_5]^+$ at 1.3 V gave an *n* value of 0.9. The only product observed by cyclic voltammetry was $[Ru(bpy)_2(Cl)NO]^{2+}$, and the competitive solvation reaction shown in the scheme for the pyridyl complexes must be slow, at least in a relative sense, for the chloro complexes. The Ru product and *n* value close to 1.0 suggest that the oxidative chemistry of $[Ru(bpy)_2(Cl)N(O)OC_2H_5]^+$ is similar to that found for the analogous pyridyl complex.

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Registry No. $[Ru(bpy)(py)N(O)OCH_3](PF_6)_2$, 72709-12-7; $[Ru(bpy)(py)N(O)OC_2H_5](PF_6)_2$, 72709-10-5; [Ru(bpy)(py)N(O)O-*n*-C_4H_9]$(PF_6)_2$, 72709-08-1; [Ru(bpy)(py)N(O)O-*i*-C_3H_7]$(PF_6)_2$, 72709-06-9; $[Ru(bpy)_2(Cl)N(O)OC_2H_5]^+$, 72709-04-7; [Ru(bpy)$_2$(Cl)N(O)O-*i*-$C_3H_7$]$^+$, 72709-03-6; $[Ru(bpy)_2(Cl)NO](PF_6)_2$, 29102-12-3; $[Ru(bpy)_2(py)NO](PF_6)_3$, 29241-00-7.

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Kinetics of Ligand Substitution in Bis(*N*-*tert*-butylsalicylaldiminato)copper(II) in Various Alcoholic Media: Mechanism of the Solvent Path

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Stopped-flow spectrophotometry has been used to investigate the kinetics of ligand substitution in bis(*N*-*tert*-butylsalicylaldiminato)copper(II) (Cu(SA=*N*-*t*-Bu)$_2$) with *N*-ethylsalicylaldimine (HSA=*N*-Et) in various alcohols (ROH) according to Cu(SA=*N*-*t*-Bu)$_2$ + 2HSA=*N*-Et $\rightleftharpoons$ Cu(SA=*N*-Et)$_2$ + 2HSA=*N*-*t*-Bu ($K_{298} = 1.7 \times 10^5$ in MeOH). The rate of ligand substitution follows a two-term rate law, namely, rate = (k_{ROH}[ROH] + $k_{HSA=N\text{-}Et}$[HSA=*N*-Et])[Cu(SA=*N*-*t*-Bu)$_2$], although for most alcohols the ligand path $k_{HSA=N\text{-}Et}$[HSA=*N*-Et] cannot compete with the solvent path k_{ROH}[ROH]. In the presence of water an additional linear term contributes, namely, $k_{H_2O}[H_2O]$[Cu(SA=*N*-*t*-Bu)$_2$]. It is concluded from spectrophotometric equilibrium studies that the mechanism of the solvent path is made up of the following steps: (i) fast equilibrium Cu(SA=*N*-*t*-Bu)$_2$ + ROH $\rightleftharpoons$ Cu(SA=*N*-*t*-Bu)$_2$·ROH; (ii) fast proton transfer from bound ROH to the phenolic oxygen of the coordinated *tert*-butyl ligand; (iii) rearrangement in the coordination sphere with breaking of the Cu–OH(ligand) bond; and (iv) stepwise but fast substitution of the two-*tert*-butyl ligands by the ethyl ligands. Rearrangement step (iii) is presumably rate determining. It follows from the kinetic data that the intermediate Cu(SA=*N*-*t*-Bu, SA=*N*-Et) reacts faster than Cu(SA=*N*-*t*-Bu)$_2$. The observed order in k_{ROH} is MeOH > EtOH > 1-PrOH ≈ 1-BuOH > 2-Me-1-PrOH > 2-PrOH > 2-BuOH > 2-Me-2-PrOH > 2-Me-2-BuOH for the nonsubstituted alcohols ROH, whereas for substituted alcohols the differences in k_{ROH} are small. Attempts to correlate k_{ROH} with solvent parameters like fluidity, heat of vaporization, dielectric constant, pK^a_{ROH}, and σ_R*(Taft) are described. For Me$_2$SO/ROH mixtures the correlation of $k^{Me_2SO}{}_{ROH} \sim K^{Me_2SO}{}_{ROH}$ is very satisfying ($K^{Me_2SO}{}_{ROH}$ = acid dissociation constant of ROH in Me$_2$SO). It follows, therefore, that the acidity of the coordinated ROH molecules is kinetically significant. The ligand path $k_{HSA=N\text{-}Et}$[HSA=*N*-Et] can be described as a bimolecular reaction between Cu(SA=*N*-*t*-Bu)$_2$ and HSA=*N*-Et. Activation parameters as determined with a commercial stopped flow apparatus are critically analyzed and compared to those obtained with a properly thermostated device.

Introduction

In a previous contribution we reported[1] that ligand substitution in copper(II) salicylaldimines as studied by isotopic exchange in toluene follows a two-term law with $k_{obsd} = k_S + k_{ligand}[\text{ligand}]$ and resembles that observed for square-planar complexes. It was shown, however, that the apparent solvent path k_S is due to residual water and that it can only be described by $k_S = k_{H_2O}[H_2O]$. Hence, the coordinating properties of the nonpolar aprotic solvent toluene are obviously not sufficiently strong to initiate a solvent path.

The solvent path in classical square-planar substitution reactions has been studied predominantly in water, although there are data also with methanol as solvent.[2] It appeared very promising to us to extend the measurements on ligand substitution in copper(II) salicylaldimines by introducing a greater variety of solvents ranging from aprotic nonpolar ones like toluene to protic polar and aprotic polar ones like methanol and Me$_2$SO, respectively. This extension of the measurements aims, of course, at the collection of data which might allow a stepwise extrapolation of solvent rate constants k_S from nonreacting media like toluene and from moderately reacting ones to finally water as the most widely applied solvent. Since the complex under study is a copper(II) chelate system, other interesting aspects are additionally involved such as the formation and chemical nature of "solvento" intermediates with partially bonded chelate ligands and the question of how fast four-coordinate copper(II) complexes react in water-like media such as methanol as compared to the extremely fast reacting Cu^{2+} ions in water.

In the present contribution we present kinetic data obtained by stopped-flow measurements on the ligand substitution of complex I according to

Cu(SA=*N*-*t*-Bu)$_2$ + 2HSA=*N*-Et $\rightleftharpoons$
Cu(SA=*N*-Et)$_2$ + 2HSA=*N*-*t*-Bu

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