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recently reported for it by others,[5] who obtained it by the reaction of $Cs^+(SF_5)_2N^-$ with F_2.

The mechanism for the formation of **21** is clearly complex and may well be due to the formation of an intermediate anion, $SF_5NFSF_4NF^-$, in analogy to the formation of $CF_3NFCF_2NF^-$ from $F_2C{=}NF$ and F^-:

$$F_4S{=}NF \xrightarrow{F^-} \mathbf{1} \xrightarrow{F_4S=NF} \mathbf{21} + \text{other products}$$

In contrast to its chlorinated analogue, $F_4S{=}NCl$,[23] which spontaneously dimerizes to a cyclic four-membered ring compound, $(F_4SNCl)_2$,[11q] $F_4S{=}NF$ shows no tendency to form such a dimer, even when heated. In another attempt to induce dimerization, photolysis of $F_4S{=}NF$ was tried. After 1 h of ultraviolet irradiation through Pyrex glass, $F_4S{=}NF$ was recovered unchanged. Irradiation through quartz resulted in partial decomposition of $F_4S{=}NF$, with production of products similar to those found after its decomposition in the presence of KF. These included SF_4, SF_6, N_2, and, interestingly, $(SF_5)_2NF$ (**21**). In this case, the formation of **21** may proceed by a mechanism similar in many respects to that proposed by others[5a,c,d,f] for the formation of $F_4S{=}NSF_5$ from F_2 and NSF_3.

Acknowledgment. Support of this research by the National Science Foundation (Grant Nos. CHE 8116043 and 8217217) and the Army Research Office (Grant Nos. DAAG29-82-K-0188 and DAAG29-80-C-0102) is gratefully acknowledged. D.D.D. acknowledges the Alexander von Humboldt Stiftung for a fellowship during part of this research.

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(23) $SF_4{=}NCl$ has never been isolated, but it is assumed to be the precursor to the cyclic dimer.[11q]

Notes

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Chemistry of Bipyridyl-like Ligands. 3. Complexes of Ruthenium(II) with 2-((4-Nitrophenyl)azo)pyridine[1]

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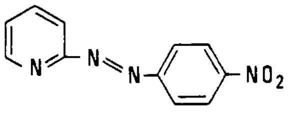
Received June 1, 1983

In recent years we have been studying the influence of π-accepting ligands on the properties of transition-metal complexes. As a ligand of this type, 2-(phenylazo)pyridine (Azpy) on ruthenium(II) has proven to be very fruitful in studies both by us[2,3] and others.[4-6] The ligand properties of Azpy have been shown to be related to the strong π-acidity of this compound; a variety of mixed-ligand complexes can be isolated,[3,5,6] and this has led to a useful infrared probe for ruthenium–ligand π-bonding.[3]

Azpy is a stronger π-acid ligand than is 2,2′-bipyridyl (bpy);[3,6] it is now of interest to us to determine the effects of even greater ligand π-accepting properties on ruthenium(II) complexes. The effect of electron-withdrawing substituents on bpy is known to further stabilize ruthenium(II).[7] However, in Azpy the phenyl ring can undergo rotation, affecting conjugation with the azo group, and thus reduce inductive effects on the metal–ligand bond.

In the present work we have attempted to demonstrate the effect of a substituent on the Azpy phenyl ring by preparing ruthenium(II) complexes of 2-((4-nitrophenyl)azo)pyridine (NAz).



NAz

NAz should be a stronger π-acid than Azpy, and this property should be reflected in its complexes. That this is indeed so is shown in the present work.

Table I. Differential Pulse Voltammetry in Acetonitrile Solutions (0.10 M $NaClO_4$) vs. Ag Wire

compd	peak potentials, V
	Anodic Scan
$[Ru(NAz)_2Cl_2]$	(α) 1.27 (137),[a] (β) 1.22 (142), (γ) 1.07 (137)
$[Ru(Azpy)_2Cl_2]$	(α) 1.11 (137), (β) 1.10 (137), (γ) 0.97 (141)
ferrocene	0.383 (135)
	Cathodic Scan
$[Ru(NAz)_3](ClO_4)_2$	0.015 (130), −0.265 (130), −0.608 (142),[b] −0.737, −0.785[c]
$[Ru(Azpy)_3](ClO_4)_2$	−0.116 (126), −0.433 (126), −0.913 (134)

[a] Peak width (mV) at half-height given in parentheses. [b] Peak not completely separated from the following one; estimated by assuming symmetrical shape. [c] Two peaks, slightly separated; half-width 134 mV.

Experimental Section

Materials. Reagents were used as received. $RuCl_3 \cdot 3H_2O$ was purchased from Matthey Bishop, Inc., Malvern, PA; organic chemicals were from Aldrich Chemical. 2-(4-Nitrophenyl)azo)pyridine was prepared as reported by Pentimalli.[8] Thin-layer-chromatography (TLC) plates were precoated TLC sheets, Silica Gel 60F-254, from EM Laboratories, Inc., Elmsford, NY.

Methods. Physical measurements were performed as previously described.[2,3] Differential-pulse voltammetry was performed with a PAR electrochemical unit, Model 170, using a three-electrode system (platinum microdisk working electrode, platinum wire counterelectrode, and silver wire reference electrodes). Spectrograde acetonitrile, 0.10 M in sodium perchlorate, was used as the solvent; solutions were degassed with nitrogen. The scan rate was 2 mV/s, and pulse height was 10 mV.

Observed peak emf values are reported in Table I. For comparison with other systems both cyclic voltammetry and differential-pulse voltammetry were performed on ferrocene under identical conditions. CV on ferrocene gave a formal potential (vs. Ag wire) of 0.324 V. Using the value of 0.400 V (NHE)[9] establishes the potential of the reference at 0.076 V.

Analyses were performed by Baron Consulting Co., Orange, CT; prior to analysis samples were redried in vacuo at 110 °C.

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Preparations. Crude [Ru(NAz)$_2$Cl$_2$]. A 2.00-g sample of RuCl$_3$·3H$_2$O and 3.36 g of NAz were mixed in 200 mL of ethanol and heated on the steam bath for 3 $^1/_2$ h. This mixture was then allowed to stand for 6 days. A dark, crystalline mass was formed, isolated by filtration, and washed with water and diethyl ether (yield 4.08 g, 88%). Shorter standing resulted in a slightly reduced yield (83% after 1 day). TLC showed this material to contain one green and two dark blue compounds (the γ-, α- and β-isomers) as the major components and several other unidentified compounds.

Separation of Isomers. γ-[Ru(NAz)$_2$Cl$_2$]. Crude [Ru(NAz)$_2$Cl$_2$] was dissolved in dichloromethane (1.500 g in 2100 mL) by heating the mixture to boiling and allowing it to cool overnight with stirring. After the residue was removed (crude γ-isomer, 0.160 g), the solution was loaded on an Al$_2$O$_3$ column (Grade I, 2.6 × 50 cm, packed in dichloromethane) and developed with 15% chloroform (0.75% ethanol stabilizer) in dichloromethane (ca. 3 L) followed by 1% ethanol in dichloromethane (ca. 1 L). The green γ-isomer eluted first with other green impurities; composition of the fractions was determined by TLC (silica plates, ethyl acetate development). Fractions containing the γ-isomer were combined and evaporated to 300 mL, and an equal volume of diethyl ether was added. After 1–2 days the complex was isolated by filtration and washed with diethyl ether (0.467 g). The blue fractions were evaporated to dryness (0.740 g).

Recrystallization of the green isomer was achieved by dissolving 0.200 g in 60 mL of warm dimethyl sulfoxide. After filtration 100 mL of water was added and the solution kept warm (50 °C) during precipitation. The complex was isolated by filtration, washed with water, and dried in vacuo over P$_4$O$_{10}$ (0.147 g). Anal. Calcd for [Ru(NAz)$_2$Cl$_2$]: C, 42.04; H, 2.57; N, 17.83; Cl, 11.28. Found: C, 42.21; H, 2.82; N, 17.59; Cl, 11.17.

β-[Ru(NAz)$_2$Cl$_2$]. The blue solid recovered from the chromatographic separation above was refluxed overnight in dichloromethane (0.640 g in 160 mL), the mixture was cooled to room temperature and filtered, the filtrate was set aside for chromatography, and the solid was washed with diethyl ether (0.330 g of nearly pure β-isomer). Recrystallization was accomplished by refluxing the solid, with stirring, for 4 h in 350 mL of dichloromethane. After filtration 400 mL of diethyl ether was added and the solution allowed to stand for several days. Filtration and washing with diethyl ether afforded, after drying in vacuo over P$_4$O$_{10}$, 0.237 g of the β-isomer (pure by TLC on silica plates, ethyl acetate developer). Anal. Found: C, 41.89; H, 2.89; N, 17.65; Cl, 11.47.

α-[Ru(NAz)$_2$Cl$_2$]. The dichloromethane solution from the extraction of the β-isomer was diluted to a concentration of 0.100 g/100 mL; 100 mL of the solution was added to 6 mL of silica gel (Silica Gel-M, Hermann Bros., Köln, West Germany; redried 3$^1/_2$ h at 115 °C) and the mixture allowed to evaporate. This mixture was slurried with ethyl acetate, allowed to stand for 45 min, and applied to a column (1.5 × 35 cm; packed in ethyl acetate); development was with ethyl acetate (400 mL) followed by 1:1 ethyl acetate–ethanol (200 mL). The first fractions contained pure α-isomer, intermediate fractions were a mixture, and the last fractions contained pure β-isomer. Evaporation of the α-isomer fractions yielded 0.04 g of complex. Recrystallization was effected by dissolving 0.310 g of complex in 150 mL of dichloromethane, filtering to remove residue, and adding 200 mL of diethyl ether. Crystallization commenced quickly. After filtration the solid was washed with diethyl ether and dried in vacuo over P$_4$O$_{10}$ (0.217 g). Anal. Found: C, 41.91; H, 2.78; N, 17.55; Cl, 11.51. TLC (silica plates, ethyl acetate developer) showed one component.

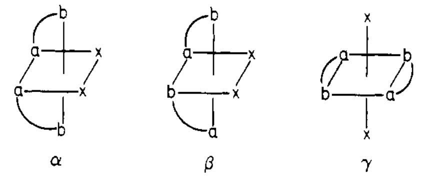
Preparation of [Ru(NAz)$_3$](ClO$_4$)$_2$. A 0.20-g sample of crude RuNAz$_2$Cl$_2$ was finely powdered and mixed with 50 mL of water containing 2 mL of concentrated HNO$_3$ and 0.324 g of silver nitrate. After stirring and refluxing for 4 h, the mixture was allowed to stand for 1 day and the residue removed by filtration (AgCl and γ-[Ru(NAz)$_2$Cl$_2$]). A 0.080-g sample of NAz was added and the solution refluxed 4 h; then 10 mL of 10% NaClO$_4$ solution was added and the solution allowed to cool with stirring overnight. The crude complex was isolated by filtration and washed once with 10 mL of water and then several times with diethyl ether (0.191 g, 61%).

For recrystallization 0.247 g of complex was dissolved in 200 mL of acetone (at room temperature), the mixture was filtered, and 50 mL of diethyl ether was added. After 6 days the complex was isolated by filtration, washed with diethyl ether, and dried in vacuo over P$_4$O$_{10}$ (0.122 g isolated). TLC (developed with 0.05 M tetraethylammonium perchlorate in acetonitrile on plastic-backed silica plates) showed only two isomers (dark orange). Anal. Calcd for Ru(NAz)$_3$(ClO$_4$)$_2$: C, 40.25; H, 2.46; N, 17.07; Cl, 7.20. Found: C, 40.48; H, 2.74; N, 17.07; Cl, 7.42.

Addition of more diethyl ether to the filtrate yielded impure complex.

Results and Discussion

Synthesis. The anticipated high π-acidity of NAz is realized in the complexes of this ligand with ruthenium(II). In general the complex chemistry is very similar to that of Azpy, differences being primarily in the degree of back-π-bonding rather than different effects. As with Azpy, three isomers of the dichloro bis complex, [Ru(NAz)$_2$Cl$_2$], are formed and have been separated. Again, thin-layer chromatography has been an excellent tool for detecting the presence of isomers and in establishing isomeric purity. We label the three isomers of [Ru(NAz)$_2$Cl$_2$] as α-, β-, and γ-forms by analogy with those of Azpy:



a = azo N; b = py N

Configurations have been related to the [Ru(Azpy)$_2$Cl$_2$] isomers by their optical spectra (see below).

We presume NAz to bond through the pyridine nitrogen and the azo nitrogen adjacent to the phenyl group, as occurs in Azpy complexes. This has been established for [Ru(Azpy)$_2$(N$_3$)$_2$] crystallographically,[10] and crystal structure results have been cited in Chakravorty's papers.[5,6] There is no indication that NAz differs from Azpy in this respect.

NAz complexes are of considerably lower solubility than those of Azpy. For that reason it was not possible to obtain NMR spectra or cyclic voltammetric data; differential-pulse voltammetry results could, however, be obtained.

γ-[Ru(NAz)$_2$Cl$_2$] undergoes isomerization as does γ-[Ru(Azpy)$_2$Cl$_2$].[2] Refluxing the compound in *m*-dichlorobenzene gives a very dilute solution; TLC shows this to produce both α- and β-isomers. Decomposition also occurs very slowly; after 1 month of reflux only the β-isomer and new, unidentified components are present. This is one difference we have observed from the chemistry of γ-[Ru(Azpy)$_2$Cl$_2$], where the ultimate product of isomerization is the cis α-form.[2]

In the two cis isomers of [Ru(Azpy)$_2$Cl$_2$] the chloride ligands could be exchanged to prepare new complexes.[3] [Ru(NAz)$_2$Cl$_2$] undergoes very inefficient chloride replacement. For example, heating it in ethanol with sodium nitrite leads to only traces of new complexes, in contrast with the synthesis of [Ru(Azpy)$_2$(NO$_2$)$_2$].[3] This poorer chloride replacement in NAz complexes is to be anticipated. The higher formal charge produced on ruthenium by bonding to a stronger π-acceptor (NAz) should slow the rate of chloride loss. Isied and Taube have demonstrated this effect of π-acid ligands on ruthenium(II) lability.[11] Also, Weiner and Basu[7] and Basu et al.[12] were unable to prepare the ruthenium(II) tris chelate of 4,4′-dinitro-2,2′-bipyridyl, presumably because of lack of reactivity in [RuL$_2$Cl$_2$] caused by the strong π-acid ligand.

Chloride removal can be effected by refluxing [Ru(NAz)$_2$Cl$_2$] with aqueous silver ion. The green γ-[Ru(NAz)$_2$Cl$_2$] is unreactive, while the cis forms are converted

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Table II. Absorption Spectra of Complexes

compd	λ_{max}, nm ($10^{-3}\epsilon$,[a] M^{-1} cm^{-1})			
NAz[b]	464 (0.621)	330 (20.4)		
α-[Ru(NAz)$_2$Cl$_2$][b]	600 (11.4)	465 (3.06)	314 (32.6)	
β-[Ru(NAz)$_2$Cl$_2$][b]	582 (11.1)	483 (sh)	320 (29.1)	
γ-[Ru(NAz)$_2$Cl$_2$][b]	654 (11.0)	386 (sh)	298 (24.4)	
[Ru(NAz)$_3$](ClO$_4$)$_2$[c]	505 (14.0)	470 (sh)	343 (35.8)	268 (38.6)

[a] Molar extinction coefficient. [b] In dimethyl sulfoxide. [c] In acetonitrile, freshly prepared solution.

into aquo complexes. From this solution the tris complex $[Ru(NAz)_3]^{2+}$ can be prepared by addition of NAz. A mixture of two isomers is thus obtained, as observed for $[Ru(Azpy)_3]^{2+}$.[3]

$[Ru(NAz)_3]^{2+}$ is not particularly stable, solid samples showing decomposition over several months. Reduction occurs readily; TLC on aluminum-backed plates always shows the presence of reduced forms, while plates with a nonreducing backing do not. Ease of reduction parallels that of $[Ru(Azpy)_3]^{2+}$; this appears to be a characteristic of ruthenium(II) complexes of strong π-acid ligands.

Optical Spectra. Absorption spectra of solutions of the compounds are reported in Table II. These appear to be typical charge-transfer (CT) spectra with extinction coefficients for the lowest band near 10^4 M^{-1} cm^{-1}. Spectra of the NAz complexes are nearly identical with those of the Azpy compounds, the NAz complexes showing a small (ca. 300 cm^{-1}) bathochromic shift from that of the corresponding Azpy complex. The strong similarity of the spectra of $[Ru(NAz)_2Cl_2]$ isomers to those of the Azpy complexes allowed us to assign structures to these compounds, consistent with all the other measurements. Figure 1 shows spectra of the three isomers with both Azpy and NAz.

The lowest energy absorption band in free Azpy (440 nm) is 1100 cm^{-1} higher in energy that that of free NAz. Assuming that the lowest band in the complexes (d-π^*) is to the upper state involved in this free-ligand transition, then the ca. 300-cm^{-1} bathochromic shift of $[Ru(NAz)_2Cl_2]$ isomers from those in the Azpy complexes still indicates a greater stabilization of the t_{2g} ruthenium orbitals in the NAz complexes. The same situation occurs between $[Ru(Azpy)_3]^{2+}$ and $[Ru(NAz)_3]^{2+}$.

Thus, the optical spectra are in keeping with NAz being a better ligand than Azpy in terms of stabilization of ruthenium(II). This is also borne out by the electrochemical measurements.

Emission spectra could be obtained from $[Ru(NAz)_3]^{2+}$ at 77 K in a methanol–ethanol glass (freezing immediately after preparation to minimize reduction). This emission is at 798 nm and appears as a single peak. Under identical conditions $[Ru(Azpy)_3]^{2+}$ emits at 763 nm. Interestingly the lifetimes of both emissions are very short; from the oscilloscope signal we estimate a mean lifetime of ca. 0.01 μs. This is significantly shorter than the lifetime of $[Ru(bpy)_3]^{2+}$ (ca. 5 μs)[13] and suggests the presence of some ligand characteristic that facilitates the nonradiative energy loss in complexes of these ligands.

Basu et al.[12] found $[Ru(NO_2\text{-}bpy)_3]^{2+}$ to be essentially nonemitting under these conditions. Their study showed the nitro group to vibrationally dissipate excited-state energy to the solvent. It was thus surprising that we were able to detect emission, of intensity comparable to that of $[Ru(Azpy)_3]^{2+}$, from $[Ru(NAz)_3]^{2+}$.

Infrared Spectra. In free NAz the N=N stretching mode appears at 1419 cm^{-1} as anticipated.[14] With strong metal–ligand back-π-bonding this mode is expected to shift dramatically to lower frequencies as observed in Azpy complexes.[2,3] Our assignments for this vibration appear in Table III; it can be seen that the α-, β-, and γ-isomers for the two ligands, NAz and Azpy, are very similar. The 100-cm^{-1} shift from the free-ligand azo mode in $[Ru(NAz)_2Cl_2]$ is taken as further evidence for pronounced metal–ligand π-bonding.

Strong R–NO$_2$ stretching modes near 1520 and 1350 cm^{-1} obscure some of the information we would hope to obtain. In $[Ru(NAz)_3](ClO_4)_2$ no azo mode is immediately apparent; this vibration is assigned as a shoulder (at 1360 cm^{-1}) on the symmetric nitro stretch at 1350 cm^{-1}. Thus, the presence of six π-acid ligating groups requires less π-bonding to each,

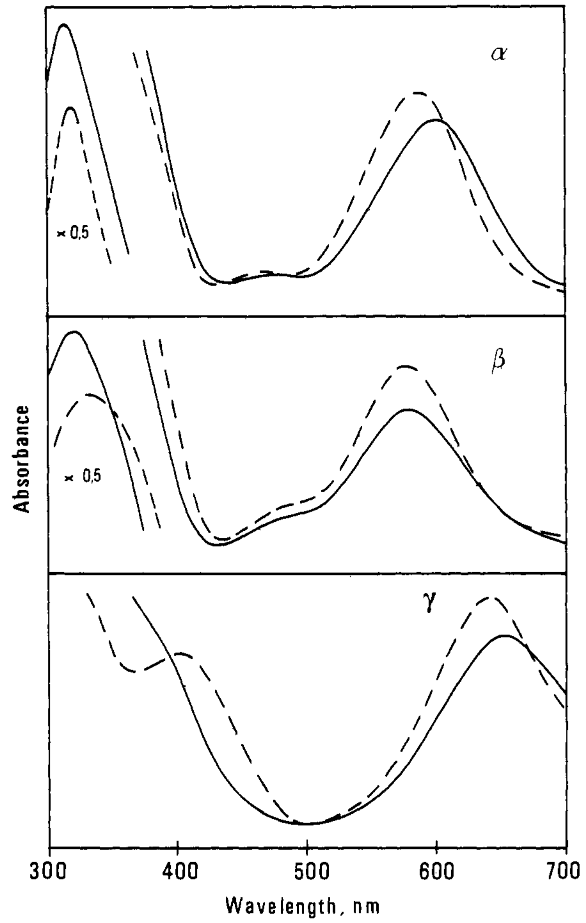

Figure 1. Visible spectra of $[Ru(NAz)_2Cl_2]$ and $[Ru(Azpy)_2Cl_2]$ isomers in dimethyl sulfoxide: (—) $[Ru(NAz)_2Cl_2]$; (---) $[Ru(Azpy)_2Cl_2]$.

Table III. Infrared Azo Stretching Modes (cm^{-1})

	[RuL$_2$Cl$_2$]			[RuL$_3$](ClO$_4$)$_2$
	α	β	γ	
NAz	1322	1327	1306	1360 (sh)
	1303	1297	1290	
Azpy[a]	1323	1317	1303	1358
	1295	1298	1290	

[a] Data reported earlier.[2,3]

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resulting in a higher wave number value than in $[Ru(NAz)_2Cl_2]$, exactly as observed for $[Ru(Azpy)_3](ClO_4)_2$.[3]

Further support for our structural assignments for the isomers of $[Ru(NAz)_2Cl_2]$ is obtained from the metal–ligand vibrational region. While spectra are of poorer quality than those of the $[Ru(Azpy)_2Cl_2]$ isomers, there is a marked similarity between the two series of compounds. As with the Azpy series, γ-$[Ru(NAz)_2Cl_2]$ has fewer bands than the α- and β-isomers, suggesting the presence of the C_{2h} symmetry required of the trans–trans isomer.[2] Assignments in this region are difficult, but we tentatively assign the Ru–Cl mode at 316 cm^{-1} in γ-$[Ru(NAz)_2Cl_2]$, at 308 and 336 cm^{-1} in the α-form, and at 306 and 328 cm^{-1} in the β-isomer, consistent with our earlier observations[2] and those of others.[15]

Electrochemical Measurements. NAz complexes were of too low solubility to obtain cyclic voltammetry measurements; however, acetonitrile solutions were sufficiently concentrated for differential-pulse voltammetry (DPV). This technique gives a peak potential slightly displaced from the formal potentials of CV measurements;[16] unfortunately no straightforward calculation of $E^{\circ\prime}$ is readily made by using finite pulse heights. Reversibility can be established from peak widths at half-height; for small pulse amplitudes a one-electron transfer should show $W_{1/2}$ of 90.4 mV.[16] The data of Table I show the known reversible ferrocene system to have $W_{1/2}$, under our conditions, of 135 mV, and this serves as our criterion of reversibility.

All isomers of $[Ru(NAz)_2Cl_2]$ showed greater stabilization of ruthenium(II) than the corresponding Azpy complexes, as anticipated. The peak potentials indicate NAz to be one of the most effective ligands for stabilizing ruthenium(II) yet reported. This most certainly is a consequence of the strong π-acceptor properties of NAz caused by the inductive effect of the nitro group. A comparable situation occurs in $[Ru((NO_2)_2bpy)_2Cl_2]$ where the potential is increased to 0.85 V, compared with 0.35 V for $[Ru(bpy)_2Cl_2]$.[7]

The observed trend in potentials of the three isomers of $[Ru(NAz)_2Cl_2]$ parallels that in the corresponding Azpy complexes, lending further support to our configuration assignments based on the optical spectra.

Strong metal–ligand π-bonding is further exemplified in $[Ru(NAz)_3]^{2+}$. Neither $[Ru(NAz)_3]^{2+}$ nor $[Ru(Azpy)_3[^{2+}$ shows electrochemical oxidation up to the solvent cutoff (ca. 2 V). Reduction of both compounds, however, is favorable, with $[Ru(NAz)_3]^{2+}$ going to its first reduced form at a peak potential of 0.015 V (ca. 0.1 V vs. NHE). Such a high reduction potential for $[Ru(NAz)_3]^{2+}$ may explain the instability of this compound in both solution and solid state. We presume $[Ru(NAz)_3]^+$ to contain a ligand-localized radical; $[Ru(Azpy)_3]^+$ shows an ESR signal characteristic of such a species ($g \approx 2.00$). Other workers have observed ligand-localized radicals in the transient $[Ru(bpy)_3]^+$.[17]

Reduction of $[Ru(NAz)_3]^{2+}$ is more complex than that of $[Ru(Azpy)_3]^{2+}$, with more peaks occurring as the sweep becomes more cathodic. This most likely is due to electrochemistry on the ligand nitro groups and has been considered no further.

Reduction of other ruthenium(II) complexes of strong π-acceptor ligands is well documented. The $[Ru(bpy)_3]^{2+/+}$ potential is −1.33 V[18] while with the stronger π-acid ligand 2,2′-bipyrazyl the $[Ru(bpz)]^{2+/+}$ potential is −0.86 V.[19] Vlček[20] has considered the stabilization of reduced ligands by coordination and points out that this is caused for the most part by the central field (positively charged) of the metal. Thus, metal–ligand back-π-bonding, which increases the metal ion effective charge, should lead to stabilization of reduced forms. It should be possible, then, to design complexes having stabilized ligand radical anions by adjusting the extent of back-π-interaction.

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Photochemistry of the *cis*- and *trans*-Dibromobis(ethylenediamine)ruthenium(III) Cations

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Irradiation of the ligand field bands of many transition-metal complexes causes ligand labilization and solvolysis, often with geometric (or optical) isomerization. The development of models to predict which of the six ligands in a given complex is photolabile has been a spirited research area,[2–6] but until recently, the stereochemical consequences of photoinduced substitutions have received less attention. Theoretical approaches to photoinduced stereochemical changes (or the lack of change) have recently been presented,[7–9] and experimental studies are exploring their validity.[10–13]

One assumption of these models[7,8] is that photoinduced substitutions can be considered to result from three consecutive events: (1) ligand loss, with a 5-coordinate complex of square-pyramid (SPY) geometry remaining, (2) intramolecular rearrangement of the 5-coordinate species to the lowest energy configuration, and (3) nucleophilic attack by water. The most stable geometry for the 5-coordinate excited state is calculated and depends on the electronic structure of the metal and the σ- and π-donor properties of the five ligands. The possibility that the three steps may be concerted is recognized,[7] but the

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