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Nitric Oxide Photorelease from Ruthenium Salen Complexes in Aqueous and Organic Solutions

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The complexes [Ru(salen)(NO)Cl] and $[Ru(salen)(NO)(H_2O)]^+$ were shown to release the nitrosyl ligand as nitric oxide upon exposure to visible light in organic and aqueous solutions respectively, by means of UV–visible, EPR, and FTIR spectroscopies. The former was prepared by a new synthetic route and had its structure determined by single-crystal X-ray diffraction. A crystal of the dichloromethane solvate is orthorhombic, space group *Fdd*2 (No. 43) and formula $C_{16}H_{14}ClN_3O_3Ru{\cdot}CH_2Cl_2$, with $Z = 16$ and cell parameters $a = 25.489(4)$, $b = 33.435(4)$, and $c = 9.3716(9)$ Å. The electronic absorption spectra of the complexes were calculated using the INDO/S method. The water-soluble complex is a potential drug for antitumoral phototreatment.

Introduction

Nitric oxide may act as a regulatory molecule in mammals. It is generated by specific enzymes and is present in various types of cells, having response to vascular, neural, and inflammatory stimuli. As low levels of nitric oxide lead to health problems, the development of drugs that can supply nitric oxide is of great interest. One approach to solve the problem is phototherapy using molecules that could liberate nitric oxide upon light irradiation. There are reports[1−4] of chemical and biochemical studies related to the nitric oxide photorelease from synthetic molecules, particularly from metal complexes.[5] Solutions containing *trans*-$[Ru(NH_3)_4(NO)X]^{3+}$ when irradiated in the 310−370 nm range release NO and generate *trans*-$[Ru(NH_3)_4(H_2O)X]^{3+}$.[6] The relationship between the in vitro photoproductivity and the in vivo biological activity of these nitrosyl complexes is being studied aiming at their use in phototherapy.[5] Ford has been working with nitrosylmetalloporphyrins including ferriheme.[2,7] Carter[4] has determined quantum yields and kinetic parameters for the photorelease of nitric oxide of $[Ru(NO)Cl_3]$ in the determination of the relaxation of vascular smooth muscles.[8−10]

The controlled photorelease of nitric oxide[11] from thermostable species of low lability can be achieved in specific biological targets by the control of irradiation region and intensity (using optical fibers and laser).[5]

Our spectroscopic studies revealed a nitric oxide photorelease from the irradiation of the ruthenium nitrosyl complexes [Ru(salen)(NO)Cl] (chloro complex) and $[Ru(salen)(NO)(H_2O)]^+$ (aquo complex) (H_2salen = bis(salicylaldehyde)ethylenediimine) in organic and aqueous solutions, respectively. This photochemical behavior was observed during the synthesis of the chloro and aquo complexes prepared for use in epoxidation[12,13] and Diels−Alder[14]

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10.1021/ic011273d CCC: $22.00

Table 1. Crystal Data and Structure Refinement for $[Ru(salen)(NO)Cl]\cdot CH_2Cl_2$

empirical formula	$C_{16}H_{14}ClN_3O_3Ru\cdot CH_2Cl_2$
fw	517.75
temp	293(2) K
wavelength	0.710 69 Å
cryst system, space group	orthorhombic, *Fdd*2 (No. 43)
unit cell dimens	$a = 25.489(4)$ Å
	$b = 33.435(4)$ Å
	$c = 9.3716(9)$ Å
unit cell vol	7986.8(16) $Å^3$
Z, calcd density	16, 1.722 g/cm^3
abs coeff	12.09 cm^{-1}
R’s[a] for “observed” data $[I > 2\sigma(I)]$[20]	R1 = 0.0399, wR2 = 0.0629
R’s[a] for all data[20]	R1 = 0.0666, wR2 = 0.0745

[a] $R(obsd) = \Sigma|F_o^2 - F_o^2(mean)|/\Sigma F_o^2$ and $R(all) = \Sigma[\sigma(F_o^2)]/\Sigma[F_o^2]$.

reactions, respectively. A new synthetic route for the chloro and aquo complexes has also been developed. During the course of this work, Ford[15] reported the photorelease of nitric oxide from the chloro complex in organic solutions. The aquo complex is thermostable, water soluble, and kinetically inert under the physicochemical conditions of the human body and could potentially be used for the development of a new generation of phototherapeutic drugs.[5]

Experimental Section

Infrared Spectroscopy. Fourier transform infrared (FTIR) spectra were recorded in the 400−4000 cm^{-1} region using a Bomem-Hartmann Braun BM series spectrophotometer. The samples were prepared in KBr pellets.

EPR Spectroscopy. Electron paramagnetic resonance (EPR) spectra were recorded in a Bruker ESP 300 E spectrometer, operating in X band (∼9.7 GHz), using a modulation field of 100 kHz. The samples were analyzed inside standard quartz tubes at 77 K.

UV−Visible Spectroscopy. UV−visible spectra in the 190−820 nm range were recorded using an HP 8452 A diode array spectrophotometer. The sample solutions were analyzed inside standard quartz cells with 1 cm path length.

Materials. All chemicals used were of reagent grade or comparable purity. Commercially available argon (White Martins) was passed through a drying column and through a deoxygenating column of MnO prior to use. Dichloromethane (Carlo Erba), methanol (Merck), dimethylformamide (OmniSolv), acetonitrile (Aldrich), ethylenediamine (Merck), and salicylaldehyde (Merck) were dried and distilled prior to use by standard methods.[16] The solid reagents $RuCl_3\cdot 3H_2O$ (Strem), $AgNO_3$ (Aldrich), and silica gel (Merck, 0.05−0.20 mm) were used without treatment. The reagent NaH, 60% in Nujol (Aldrich), was washed three times with dry hexane under argon prior to use. The compounds H_2salen and $[Na_2(salen)]$ were prepared according to published procedures.[17,18]

Crystallographic Studies. Crystals of the chloro complex were grown for crystallographic analysis from a dichloromethane solution. Experimental details are in Table 1.

After preliminary photographic examination, a crystal was mounted on a Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters and measurement of diffraction intensities (3077 unique reflections to $\theta_{max} = 30°$; 2111 were “observed” with $I > 2\sigma_I$). During processing, corrections were applied for slight crystal deterioration, Lorentz−polarization effects, and absorption (by semiempirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). The structure was determined by the automated Patterson routines in the SHELXS program[19] and refined by full-matrix least-squares methods, on F^2’s, in SHELXL[20] Hydrogen atoms were included in idealized positions; those on the salen ligand were later refined freely, but those in the solvent were set to ride on the parent carbon atom. The non-hydrogen atoms were refined with anisotropic thermal parameters, the hydrogen atoms isotropically. In the final difference map, the highest peaks (to ca. 0.44 e $Å^{-3}$) were close to the Ru atom.

Scattering factors for neutral atoms were taken from ref 21. Computer programs used in this analysis have been noted above or in Table 4 of ref 22 and were run on a DEC-AlphaStation 200 4/100 in the Biological Chemistry Department, John Innes Centre.

Syntheses. The complexes [Ru(salen)(NO)Cl] and $[Ru(salen)(NO)(H_2O)](NO_3)$ were synthesized by following methods developed in this work. The procedures used Schlenk type glassware and were performed under oxygen-free argon unless otherwise specified.

Preparation of [Ru(salen)(NO)Cl]. $RuCl_3\cdot 3H_2O$ (3 mmol) was added to a solution of $[Na_2(salen)]$ (3 mmol) in dry dimethylformamide (30 mL). The mixture was kept under reflux for 20 h, with constant stirring, after which a dark green solution developed. Nitric oxide was bubbled through the solution for 2 h under reflux resulting in a reddish brown solution. The dimethylformamide was then vacuum distilled out of the reaction flask leaving a brown residue. From this point on the procedures were performed under air. The brown residue was dissolved in dichloromethane (40 mL), and the solution was passed through quantitative filter paper. Some 30 mL of dichloromethane was removed from the filtrate leaving a red brown solution of some 10 mL. This latter solution was chromatographed in a silica column using a mixture of methanol−dichloromethane (5/95 v/v). The complex of interest was present in the red brown fraction that was collected and concentrated under vacuum to a volume of 30 mL. Hexane (1 mL) was then added, and the solution was cooled at 5 °C for 24 h during which precipitation of a crystalline brown solid occurred. The solid was filtered out and washed with hexane. Yield: 40% based on ruthenium. Analysis. Calcd for $[Ru(salen)(NO)Cl]\cdot CH_2Cl_2$: H, 3.11; N, 8.12; C, 39.44. Found: H, 3.12; N, 8.40; C, 40.30. See Infrared Spectra section for a list of relevant absorption bands.

Preparation of $[Ru(salen)(NO)(H_2O)](NO_3)$. The complex [Ru(salen)(NO)Cl] (1.2 mmol) was dissolved in 40 mL of a dichloromethane−acetone mixture (3/2 v/v), and the solution was mixed with a solution of 2 mmol of silver nitrate in 20 mL of acetone. This mixture was stirred for 3 h in the dark, and then it was slightly warmed. The mixture was filtered, four times, through Celite plugs. The filtrate was then concentrated (to 60% of the initial volume) under vacuum. Hexane (20 mL) was added to this concentrate, and

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the mixture was kept at 5 °C for 24 h during which a brownish red solid formed. The solid was filtered out, washed, and dried. Yield: 90% based on ruthenium. Anal. Calcd for $[Ru(salen)(NO)(H_2O)](NO_3)\cdot H_2O$: H, 3.66; N, 11.31; C, 38.79. Found: H, 3.40; N, 10.77; C, 36.70. See Infrared Spectra section for a list of relevant absorption bands.

Generation of Photoproducts for FTIR Analysis. The chloro complex was dissolved in degassed dichloromethane. The brown solution was irradiated with light, from a mercury lamp, for 2 h under argon, and it turned green. The solvent was stripped from the mixture by a stream of argon leaving a solid green residue that was kept inside a desiccator for 24 h before the preparation of the KBr pellet. The same procedure was used for the aquo complex using ethanol instead of dichloromethane. The color changes were also similar. The pellets were prepared under air.

Generation of Photoproducts for EPR Analysis. The chloro complex was dissolved in dichloromethane, transferred to a standard quartz EPR tube, and irradiated with UV light for 20 min prior to the recording. The same procedure was used for the aquo complex using methanol as solvent. The procedures were performed under argon.

Generation of Photoproducts for UV−Visible Analysis. The chloro complex was dissolved in acetonitrile in a concentration of 10^{-5} mol L^{-1}, and the solution was placed in a quartz cuvette with 1 cm path length. The solution was irradiated either with sunlight or with a 200 W mercury lamp. An analogous procedure was used for the aquo complex using aqueous buffer as solvent. Successive spectra were taken to monitor the photolysis. The procedures were performed under argon.

Computational Details

The electronic structures of the complexes were studied with single point calculations. The geometry of the [Ru(salen)(NO)Cl] species was obtained from X-ray atomic coordinates (Supporting Information Table S1). The geometry of the $[Ru(salen)(H_2O)_2]^+$ species (Supporting Information Table S2) was obtained from the former geometry by replacing the axial ligands NO and Cl by H_2O using the Hyperchem interface.[23] The electronic structure was calculated with the INDO/S method of Zerner and co-workers:[24] the reference determinant was obtained at the SCF level using the intermediate neglect of differential overlap (INDO) Hamiltonian of Pople,[25] and subsequent configuration interaction (CI) calculations simulated the electronic spectrum. Bulk solvent effects, for the singlet [Ru(salen)(NO)Cl] species, were included with the self-consistent reaction field (SCRF) approximation as described elsewhere.[26]

All calculations have been carried out with the ZINDO code[27] running under FreeBSD operational system in a CyberMax personal computer.

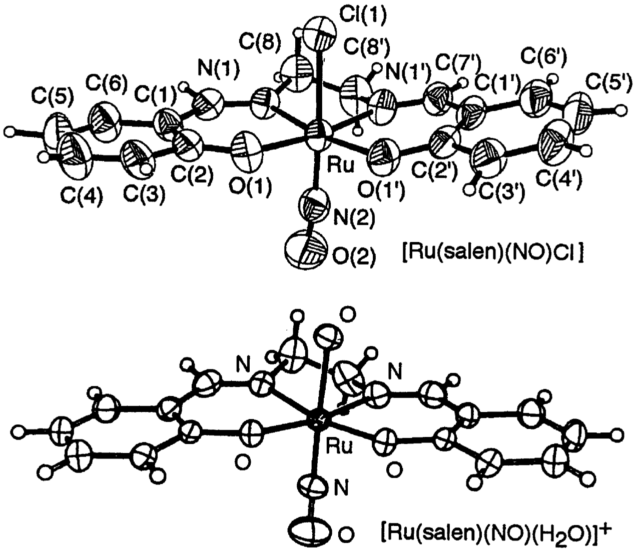

Figure 1. Top: ORTEP diagram for [Ru(salen)(NO)Cl], with heavy-atom labeling. Bottom: ORTEP diagram for $[Ru(salen)(NO)(H_2O)]^+$ adapted from ref 17 with permission. Ellipsoids are drawn to the 50% probability level.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for the Chloro Complex [Ru(salen)(NO)Cl] and for the Aquo Complex $[Ru(salen)(NO)(H_2O)]^+$ [17] with Standard Deviations in Parentheses

	chloro	aquo
Ru−N(2)	1.728(6)	1.718(7)
N(2)−O(2)	1.149(7)	1.142
Ru−N(1)	2.012(4)	2.039(5)
Ru−N(1)	2.013(5)	2.000(6)
Ru−O(1)	2.034(4)	2.034(5)
Ru−O(1)	2.030(4)	2.020(4)
Ru−N(2)−O(2)	173.7(5)	176.3
Ru−Cl(1)	2.3537(16)	
R−O(H_2O)		2.059(5)

Results and Discussion

Crystal Structure. The chloro complex crystallized as a dichloromethane solvate. The molecular structure of the chloro complex (Figure 1, top) is very similar to that of the published aquo complex (Figure 1, bottom). Table 2 has selected parameters of both complexes. The four salen atoms N(1), N(1′), O(1), and O(1′) in the chloro complex define an equatorial plane with the chloro and nitrosyl ligands in the axial positions of a slightly distorted octahedral coordination pattern. The Ru atom is displaced 0.128(2) Å toward the nitrosyl ligand from the equatorial plane.

The bond distances Ru−NO and N−O for the chloro complex are in accordance with those found for other ruthenium nitrosyl complexes[28−32] such as $[Ru(NO)(OH)(bpy)(py)_2]^{2+}$, 1.724(7) and 1.152(9) Å,[33] *trans*-[RuCl(NO)-

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Table 3. Selected Infrared Absorptions (cm^{-1}) of H_2salen, Chloro, and Aquo Complexes and of the Photoproducts of the Chloro and Aquo Complexes[a]

H_2salen	chloro complex	photoproduct of chloro complex	aquo complex	photoproduct of aquo complex	assgnt
	1838 (s)		1855 (s)	1815 (w)	ν(NO)
1635 (s)	1640 (s)	1628 (s)	1635 (s)	1614 (s)	ν(CN)
1493 (s)	1463 (m)	1462 (m)	1465 (m)	1465 (m)	ν(C−C)
1281 (s)	1298 (S)	1290 (s)	1298 (s)	1285 (S)	ν(C−C−O)
857 (s)	902 (m)	895 (m)	902 (m)	899 (m)	δ(C−H)
645 (w)	625 (w)	614 (w)	629 (w)	610 (w)	δ(C=C)

[a] Abbreviatoions: s = strong; m = medium; w = weak; ν = stretching; δ = angular deformation.

(cyclam)]$^{2+}$, 1.747(4) and 1.128(5) Å,[11] and [RuCl$_3$(NO)(AsPh$_3$)$_2$], 1.729(7) and 1.151(9) Å.[34] The relatively short bonds Ru−NO and N−O and the Ru−N−O angle not distorted greatly from linearity are indicative of a multiple bond between Ru(II) and nitrosonium (NO$^+$) and not of a single bond between Ru(III) and nitrosyl (NO). The latter situation would lead to a bent Ru−N−O angle.[35] A Ru(IV) bound to NO$^-$ is not likely since NO$^-$ usually appears as a bridging ligand.[35]

In the crystal of the chloro complex, several of the hydrogen atoms of both the salen ligand and the solvent molecule are involved in rather short intermolecular contacts; these may be described as "weak hydrogen bonds" (Supporting Information Table S3).

Infrared Spectra. In Table 3 one can see some selected infrared absorption frequencies for the free ligand H_2salen and for the chloro and aquo complexes along with their respective photoproducts. In general only small variations in absorption frequencies characteristic of the salen fragment could be noticed on going from the complexes to their respective photoproducts. Nevertheless the frequency of the CN stretch of each complex is higher than that of the respective photoproduct pointing to a major change in the ruthenium center such as a change in oxidation state. The NO stretch band has a frequency of about 1838 cm^{-1} in both complexes, and this is indicative of the linearity of the Ru−N−O bond.[36] The NO stretch is absent in the spectrum of the photoproduct of the chloro complex and has a reduced intensity in the spectrum of the photoproduct of the aquo complex. No bands around 1300 cm^{-1} were observed for the photoproducts eliminating the possible interpretation of an angular Ru−N−O coordination.[36] The similarity between the spectra of both photoproducts points to a common structure. The spectral changes on going from the complexes to the photoproducts can then be interpreted as being due to the loss of the nitrosyl ligand with a change in the formal oxidation number of the ruthenium atom from II to III.

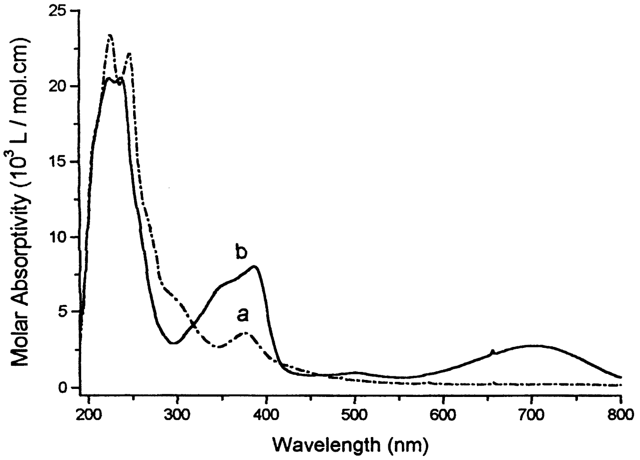

Figure 2. UV−visible spectra of complex [Ru(salen)(NO)Cl]: (a) without light irradiation (brown solution); (b) after light irradiation (green solution) (acetonitrile solution; [Ru] = 7.16 × 10^{-5} mol L^{-1}).

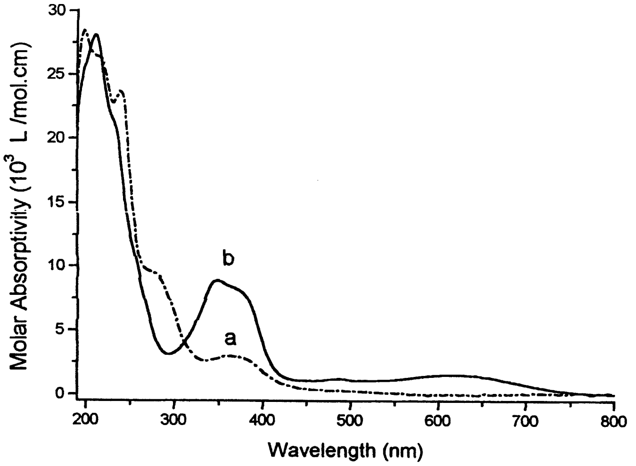

Figure 3. UV−visible spectra of complex [Ru(salen)(NO)(H$_2$O)]$^+$: (a) without light irradiation (brown solution); (b) after light irradiation (green solution) (aqueous solution; [Ru] = 4.57 × 10^{-5} mol L^{-1}).

Electronic Spectra. The electronic spectra of the chloro and aquo complexes and those of their photoproducts can be seen in Figures 2 and 3, respectively. The solutions of the chloro and aquo complexes are brown, and at 35 °C, in the dark, 6 successive spectra taken in 5 min intervals were superimposable. However, the solutions turn green upon UV−visible irradiation[37] even if kept at room temperature. The presence of isosbestic points, in the successive spectra of the irradiated solution, suggests the formation of only one photoproduct. Taken into account all spectral and computational data presented here, the photoproducts were assigned as [Ru^{III}(salen)Cl(acetonitrile)]$^+$ and [Ru^{III}(salen)(H$_2$O)$_2$]$^+$, respectively. These assignments are in accord with the observations of Ford and Works.[15]

EPR Analysis. The Ru(III) ion has electronic configuration [Kr] 4d^5, forms low-spin complexes, and in most cases the spectra of its compounds do not exhibit hyperfine or superhyperfine couplings.[38−40] According to crystal field

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(37) Since these complexes are being considered to be used as drugs for phototreatment, strong UV radiation below 360 nm was avoided due to its potential harm to human cells. Sunlight and a beam of 370 nm were used yielding similar results. See refs 2, 4, and 5.

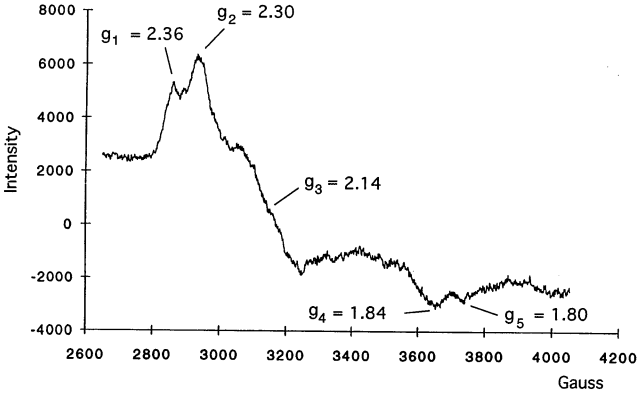

Figure 4. EPR spectrum (band X) of the photoirradiated solution of complex [Ru(salen)(NO)Cl] in dichloromethane at 77 K.

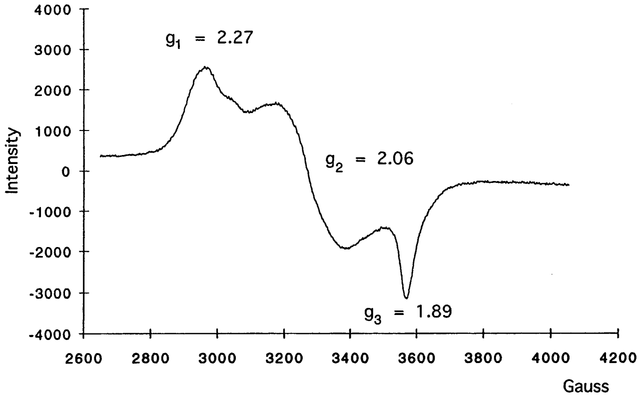

Figure 5. EPR spectrum (band X) of the photoirradiated solution of complex $[Ru(salen)(NO)(H_2O)]^+$ in methanol at 77 K.

theory the ground state of Ru(III) in an octahedral symmetry has configuration $(t_{2g})^5$ with a ground term $^2T_{2g}$, being able to act as a strong acceptor.

The EPR spectra of the photoproducts of the chloro and aquo complexes, in frozen solution at 77 K, can be seen in Figures 4 and 5, respectively. Measurements with frozen solutions were preferred over those on pure solids due to increased resolution in d^5 systems.[38]

The spectrum of the photoproduct of the chloro complex (Figure 4) apparently has one set of axial g values (g_1 and g_5) from a minor species and one set of rhombic g values (g_2, g_3, and g_4)[41] from a major species. These species can be assigned to ruthenium(III)−salen complexes not bound to NO, but their exact stoichiometry has not yet been detemined. It is possible that the rhombic spectrum corresponds to the five coordinate molecule [Ru^{III}(salen)Cl] and that the axial spectrum arises from dimers of [Ru^{III}(salen)Cl] bridged by a chloro ligand. In the dimer the Ru−Ru separation may be estimated as being greater than 4 Å (see distance Ru−Cl in Table 2) preventing bonding between these two metal ions.[41] Using the **g**-matrix treatment[42] we have assigned the rhombic spectrum as $g_2 = g_x = -2.30$, $g_3 = g_y = -2.14$, and $g_4 = g_z = -1.84$.

Table 4. INDO/S+SCRF Calculated Spectrum for the [Ru(salen)(NO)Cl] Complex in CH_3CN

transn	character	abs (nm)	oscillator strength
1 → 2	salen → NO	495[a]	0.002
1 → 3	salen → NO	437[a]	0.012
1 → 4	salen → NO	418[a]	0.003
1 → 5	MLCT	383[a]	0.001
1 → 6	MLCT	379[a]	0.001
1 → 7	salen $\pi-\pi^*$	354[b]	0.227
1 → 8	salen $\pi-\pi^*$	346[b]	0.234
1 → 9	salen $\pi-\pi^*$	308[c]	0.038
1 → 10	MLCT	307[c]	0.039
1 → 11	MLCT	295[c]	0.030
1 → 12	MLCT	279[d]	0.343
1 → 13	MLCT + IL	274[d]	0.249
1 → 14	MLCT	274[d]	0.158
1 → 15		269	0.039
1 → 16		267	0.043
1 → 17	salen $\pi-\pi^*$	261[e]	0.448
1 → 18		248	0.122
1 → 19		246[f]	0.215
1 → 29		161	2.540

[a] Weak, broad absorption observed between 500 and 400 nm. [b] Medium band with maximum = 370 nm. [c] Medium-weak band around 300 nm. [d] Series of shoulders at 260 nm. [e] Strong band at 250 nm. [f] Strong band at 220 nm.

The spectrum of the photoproduct of the aquo complex (Figure 5) has one apparent set of g values, but simulations with only one species were not able to reproduce it. Consequently at least two very similar rhombic species are present. Theses species were tentatively assigned as $[Ru(salen)(H_2O)(methanol)]^+$ and $[Ru(salen)(methanol)_2]^+$, where an axial ligand is replaced by a solvent molecule.[43] Assuming only one species and using the **g**-matrix treatment,[42] we have assigned the spectrum as $g_1 = g_x = -2.27$, $g_2 = g_y = -2.06$, and $g_3 = g_z = -1.89$. Similar g values were also observed in Ru(III) complexes with other Schiff bases.[44]

Quantum Mechanical Calculations. To verify that the formulations for the precursor and photoproduct complexes are consistent with their observed electronic spectra, we have calculated the spectra of the singlet species [Ru(salen)(NO)Cl] and the doublet species $[Ru(salen)(H_2O)_2]^+$. The former complex represents a precursor, and the latter represents a photoproduct.

Calculated Spectrum of [Ru(salen)(NO)Cl]. The SCF reference determinant shows that highest occupied MOs (nos. 57−63) have mostly ligand character, although MO no. 60 (HOMO-4) is predominantly Ru 4d. The same holds for LUMOs nos. 64−72, with MO no. 68 being almost exclusively Ru 4d. This was the active space in our configuration interaction (CIS) calculation.

Table 4 has the calculated spectrum of the chloro complex in acetonitrile. We will compare this with the experimental UV−visible spectrum of Figure 2a. The low-energy region of the calculated spectrum is dominated by a sequence of very weak, mostly salen ($\pi-\pi^*$) transitions mixing with very

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little MLCT Ru to π^*(salen) and Ru to π^*(NO). We include in this the five low-lying transitions calculated at 495, 437, 418, 383, and 379 nm. They should correspond to the very weak, broad structure observed between 500 and 400 nm. The first intense transitions are the two ligand excitations (also mixed with very little LMCT excitations) calculated at 354 and 346 nm, corresponding to the absorption observed at about 370 nm. The next significant transitions are three medium-weak excitations, mostly ligand excitations with some minor contribution from Ru d−d* excitations, probably corresponding to the weak, broad absorption centered at 380 nm. Next the calculated spectrum shows a sequence of intense absorptions calculated at 279, 274, and 274 nm. All of these match the shoulders in the same region of the observed spectrum. Next there is a strong band at 261 nm, probably corresponding to the intense absorption near 250 nm. Next there is another intense absorption at 246 nm, matching the band at 220 nm. Finally, it is easily recognizable that the oscillator strengths listed in Table 4 reproduce very well the observed bands. This calculated spectrum is therefore likely to provide a good basis for the evaluation of properties such as static and frequency-dependent hyperpolarizabilities. The low intensity (15−50 L mol^{-1} cm^{-1}) charge-transfer band Ru to π^*(NO), expected to be between 400 and 450 nm,[29,38,45] was calculated to be mixed with more intense transitions. The present assignment is in agreement with previous qualitative interpretations given to related systems.[44−46]

The spectrum of the singlet species [Ru(salen)(NO)-$(H_2O)]^+$, in Figure 3a, can be interpreted by analogy to that of Figure 2a described above.

Calculated Spectrum of [Ru(salen)$(H_2O)_2]^+$. The spectrum of the photoproduct of [Ru(salen)(NO)$(H_2O)]^+$, obtained in water, can be seen in Figure 3b. The EPR spectrum (Figure 5) exhibits a signal consistent with a doublet species. The spectrum of the doublet species [Ru^{III}(salen)$(H_2O)_2]^+$, assumed to be the photoproduct's formulation, was calculated at the ROHF level using the INDO/S method. The open-shell orbital is mostly Ru 4d.

Table 5. INDO/S Calculated Spectrum for the [Ru(salen)$(H_2O)_2]^+$ Complex

transn	character	abs (nm)	oscillator strength
1 → 2	Ru d−d*, MLCT	1694	0.002
1 → 3	Ru d−d*	1533	0.000
1 → 4	MLCT	531[a]	0.003
1 → 5	Ru d−d*	494[b]	0.005
1 → 6		477	0.011
1 → 7	Ru d−d	459	0.027
1 → 8	Ru d−d, MLCT	397[c]	0.106
1 → 9	LMCT	375	0.005
1 → 10	MLCT, salen $\pi-\pi^*$	367	0.029
1 → 11	MLCT, salen $\pi-\pi^*$	345[d]	0.094
1 → 12	MLCT, salen $\pi-\pi^*$	336[d]	0.140

[a] Weak, broad absorption observed between 700 and 400 nm. [b] Very weak band at maximum = 490 nm. [c] Medium-weak band around 390 nm. [d] A slightly stronger absorption at 340 nm.

Most of the calculated electronic spectrum (Table 5) involves strong CI mixing, and therefore, all bands exhibit contamination from other states. The calculated spectrum has two very weak, lowest energy transitions, at 1694 and 1533 nm, Ru d−d* being the major component, that are not observed in the spectrum of Figure 3b. The wavelengths of these transitions, calculated from INDO/S, should not correspond to those predicted from the EPR d^5 **g**-matrix treatment because the former transitions are d−d* heavily mixed with other components whereas the latter are assumed to be pure d−d*. The major component of the low-energy band (observed 620 nm, calculated 531 nm) is MLCT (Ru(III) to salen) that contributes with less than 16%. This transition is heavily mixed with smaller contributions from other components. The difference between the calculated and the observed wavelength is interpreted as a limitation of the INDO/S technique in nailing the absorptions characterized by strong charge transfer.[47] This band has been previously assigned qualitatively as LMCT, salen to Ru(III), in other Ru(III) salen complexes.[15,44] The next, very weak band (observed 490 nm, calculated 494 nm) is assigned to Ru d−d* strongly mixed with MLCT transitions. The system observed between 400 and 300 nm is assigned to a Ru d−d* (observed 390 nm, calculated 397 nm) and a MLCT transition (observed 340 nm, calculated 336 nm). Both transitions borrow intensity from excitations within the manifold of the salen ligand, which can explain their observed oscillator strengths. It is clear that the INDO/S calculated spectrum (Table 5) matches the observed spectrum of Figure 3b very well.

In summary, we feel quite confident to offer the calculated INDO/S spectrum, in addition to the EPR spectrum, in support to the proposition that the observed spectrum in water is due to the doublet [Ru^{III}(salen)$(H_2O)_2]^+$ species.

The spectrum shown in Figure 2b can be assigned to the doublet species [Ru^{III}(salen)Cl(acetonitrile)]$^+$ and can be interpreted by analogy to that of Figure 3b, described above, if we assume that the axial ligands play a small role.

Conclusions

The complexes [Ru^{II}(salen)(NO)Cl] and [Ru^{II}(salen)(NO)-$(H_2O)]^+$ were found to release the nitrosyl ligand, as nitric oxide, upon UV−visible light irradiation of their solutions. The major complex photoproducts were assigned as [Ru^{III}-(salen)(solvent)(axial)] (axial = chloro or aquo; solvent = water, methanol, or acetonitrile) and/or [Ru^{III}(salen)(solvent)$_2]^+$ (based on UV−visible, EPR, and FTIR spectroscopic data). A five-coordinated species [Ru^{III}(salen)(Cl)] and a chloro-bridged dimer were suggested as photoproducts in dichloromethane. The salen fragment of the precursor must be very similar to that of the photoproduct, because no major differences in salen IR frequencies were found when comparing their spectra. The major photoproducts present a rhombic structure around the Ru(III) center, as indicated from EPR data, whereas the axial species formed in dichlo-

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romethane was assigned to the dimer. The calculated spectra of the species [Ru^{II}(salen)(NO)Cl] and [Ru^{III}(salen)(H_2O)$_2$]$^+$ are in good agreement with the observed spectra. The new alternative route for the synthesis of the chloro complex gave yields of 40% based on ruthenium. The aquo complex was successfully isolated as a nitrate salt with a 90% yield. The respective bond distances and bond angles in the [Ru(salen)(NO)] fragments of the chloro and aquo complexes are very similar, as found from X-ray data, and the almost linear Ru−N−O angle points to a Ru(II) bound to a NO^+ ligand. The nitrate salt of the aquo complex is a potential drug for phototreatment since it is soluble in water, photoreleases NO above 350 nm, and is thermally and kinetically stable below 35 °C.

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Supporting Information Available: A CIF file containing crystallographic data (excluding structure factors) for the chloro complex and Tables S1−S3, listing the Cartesian coordinates of the two species submitted to quantum mechanical calculations and short intermolecular contacts of the chloro species. This material is available free of charge via the Internet at http://pubs.acs.org. The CIF file has also been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 147165. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax +44 1223 336033; e-mail deposit@cdc.cam.ac.uk).

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