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Photochemical Oxidation Reaction of Tribromobis(diethyl sulfide)nitrosylruthenium(II), $[Ru(NO)Br_3(Et_2S)_2]$: Reaction and Structural Chemistry

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The complex tribromobis(diethyl sulfide)nitrosylruthenium(II), $[Ru(NO)Br_3(Et_2S)_2]$, undergoes a photochemical oxidation reaction from which the compounds tribromo(diethyl sulfide)(diethyl sulfoxide)nitrosylruthenium(II), $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$, and bis($\mu$-bromo)bis[dibromo(diethyl sulfoxide)nitrosylruthenium(II)], $[Ru(NO)Br_3(Et_2SO)]_2$, have been isolated. The first step in the reaction is photochemical and involves the loss of NO from some of the starting material, producing a Ru(III) diethyl sulfide complex. The liberated NO together with dioxygen oxidizes a sulfide ligand on the starting material to give $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$, and after some time the insoluble dimeric ruthenium complex $[Ru(NO)Br_3(Et_2SO)]_2$ crystallizes out of solution. The single-crystal X-ray structure analyses of $[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$, which is monoclinic, space group $P2_1/c$, with $a = 17.893$ (3) Å, $b = 7.851$ (2) Å, $c = 16.265$ (3) Å, $\beta = 109.19$ (1)°, $V = 2157.8$ (6) Å^3, and $Z = 4$, and $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$, which is monoclinic, space group $P2_1/c$, with $a = 13.633$ (1) Å, $b = 8.514$ (2) Å, $c = 16.340$ (5) Å, $\beta = 106.56$ (3)°, $V = 1818$ Å^3, and $Z = 4$, are reported. In the first compound the two sulfides are trans to each other, and in the second compound the sulfide and sulfoxide ligands are cis to each other, with the NO trans to the sulfoxide ligand.

Introduction

The complex tribromobis(diethyl sulfide)nitrosylruthenium(II), $[Ru(NO)Br_3(Et_2S)_2]$, is reported to undergo a photochemical oxidation of the coordinated sulfide to sulfoxide.[1] An end product of the reaction is the dimeric complex bis(μ-bromo)bis[dibromo(diethyl sulfoxide)nitrosylruthenium(II)], $[Ru(NO)Br_3(Et_2SO)]_2$, whose crystal structure is reported.[1] The initial reaction, which is observed as a color change, requires radiation (e.g. sunlight), dioxygen, and some ethanol in the chloroform solvent. The insoluble dimer crystallizes from the solution after 6–8 weeks. Hence the possibility exists that other species occur as intermediates in the early stages of the reaction.

In the present investigation the early stages of the reaction are investigated, as well as the isolation and elucidation of the structures of intermediate products.

Experimental Section

Preparation of Compounds. The complexes of $[Ru(NO)X_3(L_2)]$ (X = Cl, L = i-Bu_2S; X = Br, L = Et_2S, n-Pr_2S, EtPhS, n-Bu_2S, n-BuPhS, i-Bu_2S; X = I, L = Et_2S) are prepared by methods described previously.[2] All the compounds give satisfactory elemental analysis (C and H) (Table I), and display a sharp absorption in their infrared spectra around 1846–1895 cm^{-1}, (Table I), which is assigned to the NO stretching mode of the coordinated NO^+.

The new complex $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$ is isolated from the photochemical reaction[1] and is isolated independently by treating "$RuBr_3NO$" with a diethyl sulfoxide/diethyl sulfide mixture. The mixture is obtained by treating Et_2S with N-bromosuccinamide.[3] The corresponding chloro and iodo complexes are also isolated from their appropriate reactions after exposure to sunlight or a Hg-discharge lamp for 2 weeks.

The dimers $[Ru(NO)X_3(Et_2SO)]_2$ (X = Cl, Br, I) crystallize from the appropriate reaction mixture after exposure to sunlight for 6–8 weeks. All compounds melt above 300 °C. The complexes have an absorption in the infrared at 918–925 cm^{-1} (Table I) due to the SO stretch of the sulfoxide ligand coordinated through oxygen.

The bis(sulfoxide) complexes $[Ru(NO)Br_3L_2]$ (L = Me_2SO and Et_2SO) are prepared by treating "$RuNOBr_3$" with the appropriate sulfoxide under reflux for 1.5 h. Isolation of the Et_2SO complex only occurs (and then in very small yields) when the Et_2SO (prepared by oxidizing Et_2S) is absolutely free of the sulfide.

The sulfides Et_2S and Ph_2S are obtained commercially, whereas the rest are obtained as outlined previously.[4]

Study of the Early Stage of the Photochemical Oxidation Reaction. The basic reaction is carried out by dissolving the complex $[Ru(NO)Br_3(Et_2S)_2]$ (0.18 g) in chloroform (10 mL) in the presence of air or dioxygen in a silica vessel. The solution is then allowed to stand either in sunlight for a few hours or in front of a Hg-discharge lamp for intervals of 45–90 min. The reaction is also studied in the absence of dioxygen by using degassed solvent and working either under dioxygen-free dinitrogen or in vacuo. A rapid change in color occurs from red-brown to purple. The 470–490-nm wavelength range is the most effective for the photochemistry. This is determined by studying the rate of the reaction when exposed to radiation through a range of color filters. The omission of one of the variables, viz. the radiation or dioxygen or ethanol, prevents the complete reaction from occurring;[1] e.g., after 1 year in the dark no reaction had occurred. After 40–60 days crystals of the dimeric complex $[Ru(NO)Br_3(Et_2SO)]_2$ form, by which time the color of the solution is red-brown.

Photochemical Step. After 45 min of irradiation of the complex $[Ru(NO)Br_3(Et_2S)_2]$ in chloroform (containing ethanol) with a Hg-discharge lamp a small amount of gas accumulates in the reaction vessel.[5] This occurs during the time of the initial color change. Mass spectral analysis of the gas compared with that of a blank run (i.e. chloroform and no complex), indicates a gas of mass 30 (mass range studied 0–100) produced from the reaction. A high-resolution analysis gives a mass of 29.99794, which compares with an expected value of 29.99799 for nitric oxide. The amount of gas evolved is measured in a calibrated vacuum line. Assuming the gas is only NO, the amount produced is <2% of the total amount of NO in the complex. There is no clear evidence for any other gaseous material from the reaction mixture compared with the blank.

The photochemical loss of NO is independent of the presence of dioxygen but does require the ethanol in the chloroform. In the absence of radiation, i.e. kept in the dark for 90 min, no nitric oxide is produced. The rate of formation of NO and also the amount produced increases when free diethyl sulfide is added to the reaction mixture. This also corresponds to an increase in the rate of formation of the purple color.

Crystalline tris(dialkyl sulfide)ruthenium(III) complexes containing the sulfides i-Bu_2S and n-PrPhS were isolated when the photochemical oxidation reaction is carried out in the presence of a 1 mol excess of free sulfide. The UV–visible spectra of the reaction mixtures are the same as those of the Ru(III) complexes. The analytical data on the two Ru(III) compounds isolated are as follows. Calcd for $[RuBr_3(n\text{-}PrPhS)_3]$: C, 40.7; H, 4.6. Found: C, 41.0; H, 4.4. Calcd for $[RuBr_3(i\text{-}Bu_2S)_3]$: C, 37.0; H, 7.0%. Found: C, 37.6; H, 7.3. Treatment of the Ru(III) complex $[RuBr_3(Et_2S)_3]$[6] with NO gas gives the Ru(II) complex, indicating the loss and gain of NO is reversible.

Oxidation Step. Crystals are isolated from the photochemical oxidation of $[Ru(NO)Br_3(Et_2S)_2]$, over a period of 4–6 weeks, as the solvent evaporates slowly. Chromatographic separation of the material on an activated alumina column produces the starting material and the complex $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$. Identification is achieved by ^{1}H NMR and ^{13}C NMR analysis and X-ray powder photography. The mixed sulfide/sulfoxide complex is prepared independently by reacting a mixture of Et_2S and Et_2SO with "$RuBr_3NO$". The single-crystal X-ray structural analysis described below confirms the stoichiometry.

The ^{1}H NMR spectrum of $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$ has two methylene resonances (quartets) at 3.20 and 3.03 ppm and two methyl

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(1) Fergusson, J. E.; Page, C. T.; Robinson, W. T. *Inorg. Chem.* **1976**, *15*, 2270.

(2) Fergusson, J. E.; Page, C. T. *Aust. J. Chem.* **1976**, *29*, 2159.

(3) Harville, R.; Reed, S. F. *J. Org. Chem.* **1968**, *33*, 3976.

(4) Aires, B. E.; Fergusson, J. E.; Howarth, D. T.; Miller, J. M. *J. Chem. Soc. A*, **1971**, 1144.

(5) Coll, R. K.; Fergusson, J. E.; Teow Sian Keong. *Aust. J. Chem.* **1986**, *39*, 1161.

(6) Fergusson, J. E.; Karran, J. D.; Seevaratnam, S. *J. Chem. Soc.* **1965**, 2627.

Table I. Analytical, Infrared, and Melting Point Data for Ruthenium(II) Sulfide Complexes[a]

	anal., %				IR, cm^{-1}		
	calcd		found				
compound	C	H	C	H	ν(NO)	ν(SO)	mp, °C
$[Ru(NO)Cl_3(i\text{-}Bu_2S)_2]$*	36.3	6.9	36.4	6.9	1858		97
$[Ru(NO)Br_3(Et_2S)_2]$	17.4	3.7	17.4	3.6	1854		129
$[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$	23.7	4.7	23.8	4.5	1847		90
$[Ru(NO)Br_3(EtPhS)_2]$	29.7	3.1	30.0	3.3	1872		163
$[Ru(NO)Br_3(n\text{-}PrPhS)_2]$*	32.0	3.6	32.2	3.7	1866		152
$[Ru(NO)Br_3(n\text{-}Bu_2S)_2]$*	29.0	5.5	29.3	5.3	1855		38
$[Ru(NO)Br_3(n\text{-}BuPhS)_2]$*	34.2	4.0	34.3	3.9	1870		154
$[Ru(NO)Br_3(i\text{-}Bu_2S)_2]$*	29.0	5.5	29.5	5.3	1846		117
$[Ru(NO)I_3(Et_2S)_2]$*	13.9	2.9	14.1	3.0	1844		134
$[Ru(NO)Br_3(Et_2S)(Et_2SO)]$*	16.9	3.6	14.8	3.6	1870	925	144
$[Ru(NO)Cl_3(Et_2SO)]_2$*	14.0	2.9	14.9	3.4	1895	918	>300
$[Ru(NO)Br_3(Et_2SO)]_2$	10.1	2.1	10.5	2.4	1878	919	>300
$[Ru(NO)I_3(Et_2SO)]_2$*	7.8	1.6	8.4	1.8	1846	921	>300
$[Ru(NO)Cl_3(Me_2SO)_2]$	12.2	3.1	12.5	3.0	1890	910	222 dec
$[Ru(NO)Br_3(Me_2SO)_2]$*	9.1	2.3	10.3	2.5	1894 1874	916 1122	183 dec
$[Ru(NO)Br_3(Et_2SO)_2]$*	16.5	3.4	16.7	3.2	1885	925 1055	>300

[a] An asterisk denotes new compounds.

Table II. Changes in ^1H NMR Spectra of Tribromobis(diethyl sulfide)nitrosylruthenium(II), $[Ru(NO)Br_3(Et_2S)_2]$

	chem shift, ppm								
duration	methylene protons				methyl protons				species
initial	3.28				1.47				$[Ru(NO)Br_3(Et_2S)_2]$
10 days	3.28	3.20	3.03		1.47	1.44	1.39		$[Ru(NO)Br_3(Et_2S)_2]$ + $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$
20 days		3.20	3.03			1.44	1.39		$[Ru(NO)Br_3(Et_2S)(Et_2SO)]$
2 months		3.20	3.03	2.70		1.44	1.39	1.33	$[Ru(NO)Br_3(Et_2S)(Et_2SO)]$ + Et_2SO
3 months			3.00	2.70			1.40	1.33	Et_2SO_2 + Et_2SO

resonances (triplets) at 1.44 and 1.39 ppm. The first of each pair corresponds to Et_2S and the second pair to Et_2SO.

The ^1H NMR spectrum of the reaction is measured, for the same sample, periodically over 3 months. The results and their interpretation are given in Table II and Figure 1. After 10 days the existence of both $[Ru(NO)Br_3(Et_2S)_2]$ and $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$ are evident in the NMR spectrum, and by 20 days $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$ is the dominant product. After 2 months, evidence for free Et_2SO is apparent, and by three months, the spectrum could be interpreted in terms of Et_2SO and Et_2SO_2 being the main products in solution. The absence of a spectrum of a ruthenium diethyl sulfide complex at this stage is because of the crystallization of the insoluble dimer.

The solution IR spectra of the reaction mixture also alter with time, and the strong absorption at 1860 cm^{-1} (due to ν(NO) in $[Ru(NO)Br_3(Et_2S)_2]$) splits into two bands, one at 1860 and one at 1880 cm^{-1}, over time. The intensity of the latter band increases, and it becomes the main absorption. The band is assigned to ν(NO) in the sulfide/sulfoxide complex and is confirmed by comparison with the solution IR spectrum of pure $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$. In addition, an absorption band at 935 cm^{-1} assigned to ν(SO) appears and increases in intensity over time.

The electronic absorption spectrum of the starting material consists of a weak band around 475 nm (absorptivity (M^{-1} cm^{-1}) 200), and strong charge-transfer bands at 302 (11000) and 246 nm (20000). The former is assigned to the ligand field transition $^1A_1 \rightarrow {}^1T_1$, the first spin-allowed transition, on the basis of its intensity and position. This band quickly disappears in the photochemical reaction, and new bands appear at 545 and 500 nm (1000), which are attributed to the Ru(III) complex $[RuBr_3(Et_2S)_3]$ (in the presence of excess Et_2S). After a longer time a new band appears around 480 nm (900), which is attributed to the formation of the Ru(II) complex $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$.

The oxidation of the diethyl sulfide requires dioxygen (e.g. air) after the photochemical step, and the rate of oxidation increases with the availability of dioxygen. When there is no dioxygen in the system the ^1H NMR shows no sign of oxidized material. The oxidation can be achieved, in the absence of light, when a mixture of NO and dioxygen is added to a solution of $[Ru(NO)Br_3(Et_2S)_2]$. The evidence for this comes from the ^1H NMR spectra and IR spectra of the solution, showing the presence of diethyl sulfoxide. If the NO is omitted from this reaction no oxidation occurs, hence it would appear that NO_2 is the oxidizing agent.

Oxidation of Dialkyl Sulfides. When a mixture of NO (generated from the reaction of sulfuric acid with sodium nitrite) and O_2 is passed through a chloroform solution of Et_2S, oxidation occurs readily to Et_2SO and Et_2SO_2. The evidence comes from the ^1H NMR spectra of the reaction solution (chemical shifts in ppm): Et_2S, CH_3 1.27, CH_2 2.57; Et_2SO, CH_3 1.33, CH_2 2.70; Et_2SO_2, CH_3 1.40, CH_2 2.97. Similar oxidations have been observed previously, but under somewhat different conditions.[7] When one of the reagent gases is removed, the oxidation did not occur; therefore, again NO_2 appears to be the oxidizing agent. However, irradiation of the reaction mixture when dioxygen is used alone does achieve oxidation, but the process is slower and requires a protic solvent, e.g. ethanol.[8,9] Since $[RuBr_3(Et_2S)_3]$ is produced in the photochemical reaction described above, it may be involved in the oxidation step. However, addition of traces of the complex does not assist in the oxidation of the sulfide or promote it in the absence of NO. The sulfides R_2S (R = n-Bu, Ph) and RR'S (R' = Ph; R = Me, Et, *n*-Pr, *n*-Bu) also undergo a similar oxidation reaction.

The reactions are followed by removing samples at different times for study by ^1H NMR, solution IR, UV, and visible spectroscopy. The mass spectra and amount of gaseous products produced are also measured. The reactions are also studied in the dark, after addition of a mixture of NO/O_2 to the flask.

Identification of the Reaction Products. The various reaction products in solution, or solid products isolated are identified from their ^1H NMR spectra by using a Varian T-60 spectrometer, from infrared spectra by using a Shimadzu IR-27G or Pye Unicam SP3-300 spectrophotometer, and from UV–visible spectra by using a Varian Superscan spectrophotometer. The mass spectra of the gaseous products are measured on a SMS Data Quad and AEI MS 902 mass spectrometers. A vacuum line is calibrated for volume by direct measurement and the pressure measured with a McLeod gauge calibrated with a MKS Baratron capacitance manometer. X-ray powder diffraction photographs are taken of solid materials by using a Philips Debye–Scherrer powder camera and Cu Kα radiation.

X-ray Structural Procedures. Two single-crystal X-ray structure determinations were completed at different times by using two different

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(7) Addison, C. C.; Sheldon, J. C. *J. Chem. Soc.* **1956**, 2705.
(8) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3759.
(9) Correa, P. E.; Riley, D. P. *J. Org. Chem.* **1985**, *50*, 1787.

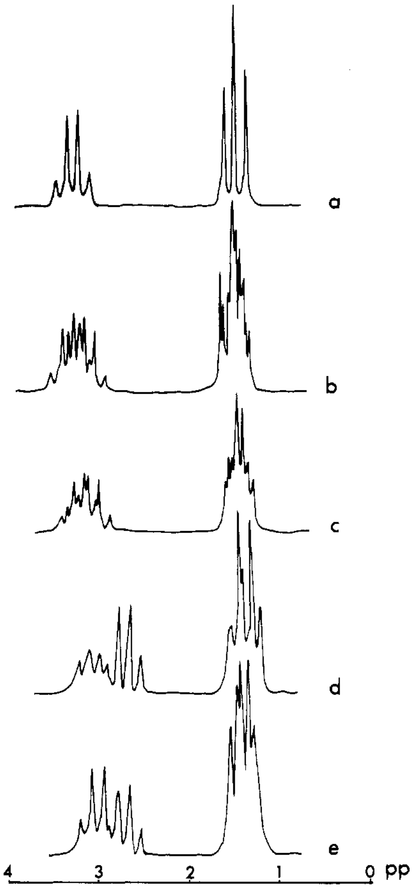

Figure 1. Changes in the ^1H NMR spectra of tribromobis(diethyl sulfide)nitrosylruthenium(II), $[Ru(NO)Br_3(Et_2S)_2]$: (a) initial, $[Ru(NO)Br_3(Et_2S)_2]$; (b) 10 days, $[Ru(NO)Br_3(Et_2S)_2]$ and $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$; (c) 20 days, $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$; (d) 2 months, $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$ and Et_2SO; (e) 3 months Et_2SO and Et_2SO_2.

X-ray diffractometers for collection of intensity data. A Hilger Watts computer-controlled four-circle diffractometer, with β filters, is used for $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$, and a Nicolet R3m four-circle diffractometer equipped with a graphite-crystal monochromator is used for $[Ru(NO)Br_3(nPr_2S)_2]$. Both structure determinations are carried out at 25 °C by using Mo Kα radiation, wavelength 0.71069 Å.

[Ru(NO)Br$_3$(*n*-Pr$_2$S)$_2$]. The cell parameters are determined by least-squares refinement using 25 accurately centered reflections (28° < 2θ < 32°). The orange-brown blocklike crystals belong to the monoclinic system; information and details of the crystal data collection are given in Table III. A total of 4288 unique reflections are collected in the hkl and $hk\bar{l}$ octants by using the θ–2θ scan technique (3° < 2θ < 50°) and a variable scan rate (6.0–29.3° min^{-1}). Crystal stability is monitored by recording three standard reflections every 100 reflections, and no significant variation is observed. Data reduction gives 3305 unique reflections of which 2419, having $I > 3[\sigma(I)]$, are used for the structure determination. Intensities are corrected for Lorentz and polarization effects, and an empirical absorption correction is applied based on ψ-scan data. Systematic absences uniquely indicate the space group $P2_1/c$.

The Ru atom and one Br atom are located by using Patterson methods and the remaining non-hydrogen atoms located from difference Fourier maps. Hydrogen atoms are included at calculated positions by using the riding model with thermal parameters equal to 1.2U of their carrier atoms. There is disorder of one Br atom (Br(3)) with the NO group. Approximate site occupancy of 0.7 for Br(3) and 0.3 for Br(3′) are deduced from relative peak heights in difference Fourier maps, and this model refines to give a site occupancy of 0.666 for Br(3) (0.333 for N′ and O′) and 0.333 for Br(3′) (0.666 for N and O). The atoms N′ and O′ are obscured in the difference maps by the large peak due to Br(3); consequently, these atoms are inserted at calculated positions and subsequently refined. Blocked-cascade least-squares refinement, including anomalous dispersion corrections,[10] converges with a conventional R value of 0.0447 (R_w = 0.0473), anisotropic temperature factors being used for all non-hydrogen atoms except N′ and O′. The function minimized is $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + 0.00052F_o^2]^{-1}$. A final difference map shows no features greater than ±0.5 electrons Å^{-3}. All the programmes used for data reduction and structure solution are included in the SHELXTL[11] (version 3.0) package. The positional parameters and temperature factors are given in Table IV, and bond length and angle data are given in Table V.

Table III. Crystal and Intensity Collection Data

param	$[Ru(NO)Br_3(Pr_2S)_2]$	$[Ru(NO)Br_3(Et_2S)(Et_2SO)]$
formula	$C_{12}H_{28}Br_3NOS_2Ru$	$C_8H_{20}Br_3NO_2S_2Ru$
fw	607.30	567.18
a, Å	17.893 (3)	13.633 (1)
b, Å	7.851 (2)	8.514 (2)
c, Å	16.265 (3)	16.340 (5)
β, deg	109.19 (1)	106.56 (3)
V, Å^3	2157.8 (6)	1818
Z	4	4
space group	$P2_1/c$	$P2_1/c$
d, g cm^{-3}		
calcd	1.869	2.07
exptl	1.82 (3)	2.06
cryst dimens, mm^3	0.78 × 0.25 × 0.31	0.37 × 0.32 × 0.20
cryst V, mm^3	0.060	0.0190
cryst mosaicity, deg	0.25	0.15
μ, cm^{-1}	64.01	80.44
transmissn factors	0.05–0.11	0.19–0.28
scan speed (2θ), deg min^{-1}	6–29.3	2.0
scan range, deg	2	1.60
2θ limit, deg	50	50
final no. of variables	199	155
no. of unique data used	2419	1585
R	0.0447	0.049
R_w	0.0473	0.058

Table IV. Final Positional Parameters (×10^4) and Temperature Factors (Å^2 × 10^3) for Tribromobis(dipropyl sulfide)nitrosylruthenium(II), $[RuBr_3NO(n\text{-}Pr_2S)_2]$

atom	x	y	z	U^a
Ru	7501 (1)	9710 (1)	34 (1)	51 (1)*
Br(1)	6212 (1)	8771 (1)	167 (1)	86 (1)*
Br(2)	8220 (1)	7824 (1)	1279 (1)	72 (1)*
Br(3)	8784 (1)	10654 (2)	−114 (1)	80 (1)*
Br(3′)	6966 (5)	11694 (14)	−1233 (5)	73 (2)*
S(1)	7521 (1)	11733 (3)	1158 (1)	58 (1)*
S(2)	7345 (1)	7211 (3)	−876 (1)	66 (1)*
C(2)	8630 (5)	13504 (11)	2490 (5)	72 (4)*
C(1)	8522 (4)	12577 (10)	1636 (5)	61 (3)*
C(3)	9471 (5)	14126 (13)	2900 (6)	90 (4)*
C(5)	6127 (6)	13564 (13)	399 (7)	108 (5)*
C(7)	8130 (6)	7003 (14)	−1337 (7)	101 (5)*
C(4)	7012 (5)	13663 (11)	670 (6)	79 (4)*
C(10)	6491 (6)	7612 (12)	−1862 (6)	101 (5)*
C(8)	8789 (6)	6006 (17)	−785 (7)	118 (6)*
C(9)	9461 (6)	5855 (16)	−1166 (7)	124 (6)*
C(6)	5835 (6)	13514 (15)	1157 (7)	126 (7)*
C(11)	6108 (6)	6026 (14)	−2313 (7)	112 (5)*
N	7033 (6)	11141 (13)	−839 (6)	69 (4)*
O	6738 (12)	11895 (37)	−1379 (15)	77 (7)*
N′	8501 (14)	10302 (28)	15 (12)	71 (6)
O′	9059 (28)	11133 (55)	−19 (26)	250 (20)
C(12)	5363 (6)	6339 (15)	−2993 (7)	132 (7)*

[a] An asterisk denotes the equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[Ru(NO)Br$_3$(Et$_2$S)(Et$_2$SO)]. The precession and Weissenberg photographs of the orange-brown, blocklike crystals, which belong to the monoclinic system with extinctions for $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n$

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(10) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(11) Sheldrick, G. M. *SHELXTL User Manual, Revision 3*; Nicolet XRD: Cupertino, CA, 1981.

Table V. Bond Lengths and Angles for Tribromobis(dipropyl sulfide)nitrosylruthenium(II), [Ru(NO)Br$_3$(*n*-Pr$_2$S)$_2$]

	Bond Lengths (Å)		
Ru–Br(1)	2.493 (1)	Ru–Br(2)	2.497 (1)
Ru–Br(3)	2.493 (2)	Ru–Br(3′)	2.508 (9)
Ru–S(1)	2.414 (2)	Ru–S(2)	2.417 (2)
Ru–N	1.787 (9)	Ru–N′	1.854 (26)
S(1)–C(1)	1.823 (7)	S(1)–C(4)	1.810 (8)
S(2)–C(7)	1.803 (12)	S(2)–C(10)	1.841 (8)
C(2)–C(1)	1.524 (12)	C(2)–C(3)	1.510 (11)
C(5)–C(4)	1.498 (13)	C(5)–C(6)	1.488 (17)
C(7)–C(8)	1.452 (14)	C(10)–C(11)	1.491 (14)
C(8)–C(9)	1.524 (17)	C(11)–C(12)	1.443 (13)
N–O	1.047 (26)	N′–O′	1.208 (55)
	Bond Angles (deg)		
Br(1)–Ru–Br(2)	89.8 (1)	Br(1)–Ru–Br(3)	179.5 (1)
Br(2)–Ru–Br(3)	90.6 (1)	Br(1)–Ru–Br(3′)	98.2 (2)
Br(2)–Ru–Br(3′)	172.0 (2)	Br(1)–Ru–S(1)	85.0 (1)
Br(2)–Ru–S(1)	84.2 (1)	Br(3)–Ru–S(1)	95.3 (1)
Br(1)–Ru–S(2)	83.6 (1)	Br(2)–Ru–S(2)	86.6 (1)
Br(3)–Ru–S(2)	96.2 (1)	S(1)–Ru–S(2)	165.4 (1)
Br(1)–Ru–N	92.9 (3)	Br(2)–Ru–N	176.8 (3)
Br(3)–Ru–N	86.6 (3)	S(1)–Ru–N	94.3 (3)
S(2)–Ru–N	95.4 (3)	Ru–S(1)–C(1)	109.3 (3)
C(1)–S(1)–C(4)	99.4 (4)	Ru–S(2)–C(7)	112.3 (3)
Ru–S(2)–C(10)	106.9 (3)	C(7)–S(2)–C(10)	100.8 (5)
Ru–N–O	175.5 (17)	Ru–N′-O′	161.8 (28)

+ 1, uniquely determine the space group as $P2_1/c$. Twelve reflections are used to obtain accurate unit cell dimensions for this crystal. The pertinent crystal formation and details of the crystal data collection are given in Table III.

The crystal displays acceptable mosaicities with ω scans, and the intensities of all the independent reflections in the *h* and *k* positive quadrant of reciprocal space for $0 < 2\theta < 50°$ are collected. Background counts are measured at both ends of the scan range with both the crystal and counter stationary. The intensities of the standard reflections are measured every 50 reflections, and all these remain statistically constant during the entire data collection.

Of the 3197 unique reflections collected only 1585 with $F_o^2 > 3\sigma(F_o^2)$ are used in subsequent solution and refinement of the structure. An absorption correction using an analytical method[12] is applied to the data set.

Direct methods are used in an attempt to obtain a correct starting model. The phases of the structure factors are derived directly from mathematical relationships.[13] The atomic positions of the RuBr$_3$ group are refined by using least-squares methods to give agreement factors of $R = 0.236$ and $R_w = 0.332$. The function minimized is $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$. A difference Fourier synthesis reveals the positions of the rest of the non-hydrogen atoms. With isotropic temperature factors the [Ru(NO)Br$_3$(Et$_2$S)(Et$_2$SO)] model converges with R and R_w at 0.080 and 0.104, respectively. In the final refinements, anisotropic thermal parameters are used for all the atoms located. No attempt is made to locate and refine the hydrogen atoms. The final agreement factors converge to 0.048 and 0.058 for R and R_w, respectively.

The highest peak in a final difference Fourier map is approximately 30% of the height of a carbon atom located earlier during this structure analysis. The observed intensities for reflections at low θ angles are systematically less than their calculated values; hence, the data are corrected for secondary extinction[14] by using the expression

$$F_o = F_o(W + (1 + W)^{1/2})^{1/2}$$

where $W = gBI_o$, g is the extinction coefficient, B is Zachariasen's angularly dependent function and I_o is the observed intensity.

A structure factor calculation on all 3197 independent reflections collected shows no large discrepancies between the $|F_c|$ and $|F_o|$ values. The positional and thermal factors are given in Table VI, and bond length and angle data are given in Table VII.

Table VI. Final Positional Parameters (×10^4) and Temperature Factors (Å^2 [Ru(NO)Br$_3$(Et$_2$S)(Et$_2$SO)] 10^3) for Tribromo(diethyl sulfide)(diethyl sulfoxide)nitrosylruthenium(II), [RuBr$_3$NO(Et$_2$SO)(Et$_2$S)]

atom	*x*	*y*	*z*	*U*[a]
Ru	2355 (1)	1893 (1)	849 (1)	50 (1)
Br(1)	854 (1)	2061 (2)	1445 (1)	74 (1)
Br(2)	3913 (1)	1917 (2)	331 (1)	85 (1)
Br(3)	3369 (1)	503 (2)	2167 (1)	72 (1)
S(1)	3869 (3)	C(111)–C(112)	1987 (2)	58 (1)
S(2)	1329 (3)	3560 (6)	−262 (2)	83 (4)
O(1)	2785 (6)	4033 (9)	1421 (5)	50 (5)
O(2)	1790 (10)	−1020 (10)	43 (9)	110 (10)
N	1981 (9)	120 (20)	350 (9)	76 (9)
C(111)	3720 (10)	4620 (20)	3086 (9)	70 (10)
C(112)	2850 (20)	5580 (20)	3120 (10)	140 (20)
N–Ru–S(2)	3970 (10)	6470 (20)	1690 (10)	90 (20)
C(122)	4190 (20)	6550 (20)	850 (10)	120 (20)
C(211)	290 (20)	2140 (30)	−890 (10)	120 (20)
C(212)	−500 (20)	2910 (30)	−1440 (10)	150 (30)
C(221)	1940 (10)	4030 (20)	−1090 (9)	90 (10)
C(222)	1630 (20)	5650 (20)	−1430 (10)	130 (20)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VII. Bond Lengths and Angles for Tribromo(ethyl sulfide)(diethyl sulfoxide)nitrosylruthenium(II), [Ru(NO)Br$_3$(Et$_2$S)(Et$_2$SO)]

	Bond Lengths (Å)		
Ru–N	1.72 (1)	S(1)–C(121)	1.81 (1)
Ru–O(1)	2.055 (8)	S(2)–C(211)	1.93 (2)
Ru–S(2)	2.412 (4)	S(2)–C(221)	1.83 (2)
Ru–Br(1)	2.509 (2)	N–O(2)	1.09 (1)
Ru–Br(2)	2.501 (2)	C(111)–C(112)	1.45 (2)
Ru–Br(3)	2.500 (2)	C(121)–C(122)	1.49 (2)
S(1)–O(1)	1.543 (8)	C(211)–C(212)	1.36 (3)
S(1)–C(111)	1.87 (1)	C(221)–C(222)	1.50 (2)
	Bond Angles (deg)		
N–Ru–O(1)	178.8 (5)	Br(2)–Ru–Br(1)	175.23 (7)
N–Ru–S(2)	97.5 (5)	O(1)–S(1)–C(111)	100.8 (6)
N–Ru–Br(3)	90.5 (5)	N–Ru–Br(1)	94.0 (4)
N–Ru–Br(2)	90.7 (4)	O(1)–Ru–S(2)	81.4 (2)
O(1)–Ru–Br(3)	90.7 (2)	C(211)–S(2)–C(221)	99.3 (9)
O(1)–Ru–Br(2)	89.3 (2)	Ru–S(2)–C(211)	102.3 (7)
O(1)–Ru–Br(1)	86.0 (2)	Ru–N–O(2)	176.5 (14)
S(2)–Ru–Br(3)	170.5 (1)	Ru–S(1)–O(1)	124.8 (5)
S(2)–Ru–Br(2)	96.1 (1)	S(2)–Ru–Br(1)	84.0 (1)
Br(3)–Ru–Br(1)	90.25 (6)	Br(3)–Ru–Br(2)	88.90 (7)

Results and Discussion

Photochemical Oxidation Reaction. From the experimental results above it is suggested that in the early stages of the reaction (45–90 min) the first step is the photochemical loss of a small amount of NO from some of the complex and the consequential oxidation of some Ru(II) to Ru(III). The reaction is also reversible and is summarized by

$$\underset{\text{red-brown}}{[\mathrm{Ru(NO)Br_3(Et_2S)_2}]} + h\nu + \text{solvent} \rightleftharpoons \underset{\text{purple}}{[\mathrm{RuBr_3(Et_2S)_2(solvent)}]} + \mathrm{NO}$$

The reaction requires a donor solvent, such as ethanol. However, if some free Et$_2$S is added to the reaction mixture, it becomes more rapid, and the sulfide replaces the solvent molecule in the product, i.e.

$$\underset{\text{red-brown}}{[\mathrm{Ru(NO)Br_3(Et_2S)_2}]} + h\nu + \mathrm{Et_2S} \rightleftharpoons \underset{\text{purple}}{[\mathrm{RuBr_3(Et_2S)_3}]} + \mathrm{NO}$$

The fact that some tris(sulfide)ruthenium(III) complexes (R$_2$S = *n*-PrPhS, *i*-Bu$_2$S) are isolated supports this suggestion.

It is then suggested that in the second step of the reaction the NO produced by the photochemical reaction together with dioxygen brings about the oxidation of diethyl sulfide to Et$_2$SO and

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(12) Program ABSORB was used; this is a locally adapted version of the program by L. Templeton and D. Templeton (described in: *Abstracts*; American Crystallographic Association: Storrs, CT, 1973; No. E10) using the analytica method of: De Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014.

(13) Program SHELX-76, a group of programs of X-ray crystallographic programs developed by G. M. Sheldrick, University of Cambridge, 1976.

(14) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558.

Et_2SO_2, the former of which coordinates to the ruthenium. The products are identified from their ^1H NMR, IR, and UV–visible spectra. The oxidation step that appears to be achieved with NO_2 is represented by the two equations

$$2NO + O_2 \rightarrow 2NO_2$$

$$[Ru(NO)Br_3(Et_2S)_2] + NO_2 \rightarrow [Ru(NO)Br_3(Et_2SO)(Et_2S)] + NO$$

This may be followed by the reaction

$$Et_2SO + NO_2 \rightarrow Et_2SO_2 + NO$$

The last two reactions allow for the regeneration of NO, which explains why oxidation of the diethyl sulfide proceeds without having to produce much nitric oxide. We conclude that the nitric oxide, produced by the photochemical reaction of the nitrosyl complex, acts as a catalyst in the oxidation of the diethyl sulfide.

Latter Stages of the Reaction. The end product of the reaction is the dimer $[Ru(NO)Br_3(Et_2SO)]_2$. It is interesting that this compound forms rather than a bis(sulfoxide) complex. Presumably the low solubility of the dimer is important in its isolation. Evidence is obtained for the existence of the complex $[Ru(NO)Br_3(Et_2SO)_2]$ from IR and ^1H NMR data, when "$RuNOBr_3$" is treated with Et_2SO absolutely free of any Et_2S. Therefore under the conditions of the photochemical oxidation reaction it appears that the formation of a bis(sulfoxide) intermediate is not favored.

Other Photochemical Oxidation Reactions. The photochemical reaction is observed to occur for the complexes $[Ru(NO)X_3(RR'S)_2]$, (X = Cl, Br; R = R' = Et, *n*-Pr, *i*-Bu; X = Br, R = Ph, R' = *n*-Bu, *n*-Pr, Et; X = I, R = R' = Et). For the two complexes $[Ru(NO)X_3(Et_2S)_2]$ (X = Cl, I), the reaction proceeds in the same manner as for the bromo complex, except that Et_2SO_2 is not observed. The reactions are followed by using ^1H NMR spectrometry and changes in the ν(NO) stretching frequency in the infrared region. For the chloro complex the ν(NO) stretch at 1870 cm^{-1} (solution IR) displays a shoulder on the high-frequency side as the $[Ru(NO)Cl_3(Et_2SO)(Et_2S)]$ compound is formed, whereas for the iodo complex the 1846-cm^{-1} band splits (similar to the bromo complex) to give a new band at 1874 cm^{-1}. In addition the ν(SO) band (925–930 cm^{-1}) appears for both compounds and grows in intensity.

The rate at which the ν(NO) band splits for the iodo and bromo complexes, over 6 days, suggests that the rate of the photochemical oxidation is greater for the bromo complex. The same trend is observed from changes in the visible spectra of the complexes (i.e. the change from Ru(II) (red-brown) to Ru(III) (purple; the photochemical step) suggests the rate is in the order Cl > Br > I. Over a longer period of time, 20–40 days, (using ^1H NMR) the order of the rate of reaction appears to be reversed, i.e. Cl < Br < I, but by this time other factors may have intervened. From both infrared and visible spectral changes it appears that the speed of the reaction also follows the orders Et_2S > *n*-Pr_2S > *i*-Bu_2S and *n*-BuPhS > n-PrPhS > EtPhS for the chloro and bromo compounds, respectively.

New Complexes. A number of new nitrosyl complexes of ruthenium have been isolated (Table I). Their spectral (IR, UV-visible and ^1H NMR) features are similar to those of reported complexes,[2,15] with a linear Ru–N–O system and sulfoxide coordinated through the oxygen atom. A few crystals of the two compounds $[Ru(NO)X_3(Et_2SO)(Et_2S)]$ (X = Cl, I) are isolated after 2 weeks of radiation of the appropriate reaction mixture. These two compounds are only identified from their ^1H NMR and IR spectra and their similarity to the bromo complex. Both of the bis(sulfoxide) complexes $[Ru(NO)Br_3L_2]$ (L = Me_2SO and Et_2SO) are prepared from "$RuBr_3NO$" and the appropriate sulfoxide. Both complexes have two ν(SO) bands in the IR region attributable to O-bonded and S-bonded sulfoxides:[16,17] 916 and 1122 cm^{-1} for the dimethyl sulfoxide complex, and 925 and 1055 cm^{-1} for the diethyl sulfoxide complex. On the other hand the chloro complex $[Ru(NO)Cl_3(Me_2SO)_2]$[16] has only one ν(SO) band at 910 cm^{-1}. The ^1H NMR spectrum of the complex $[Ru(NO)Br_3(Et_2SO)_2]$ consists of a triplet at 1.28 ppm and two sets of overlapping quartets at 2.85 and 2.69 ppm. The quartets collapse to give four singlets when the methyl protons are decoupled, suggesting four different methylene environments. The NMR spectra provide further support for one sulfoxide ligand being bonded through oxygen and one through sulfur to ruthenium.

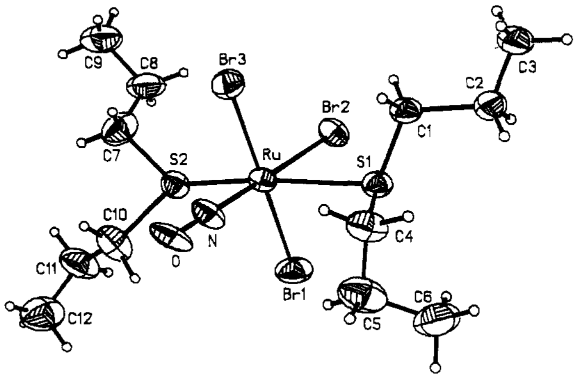

Figure 2. Perspective view of the tribromobis(dipropyl sulfide)nitrosylruthenium(II), $[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$, molecule.

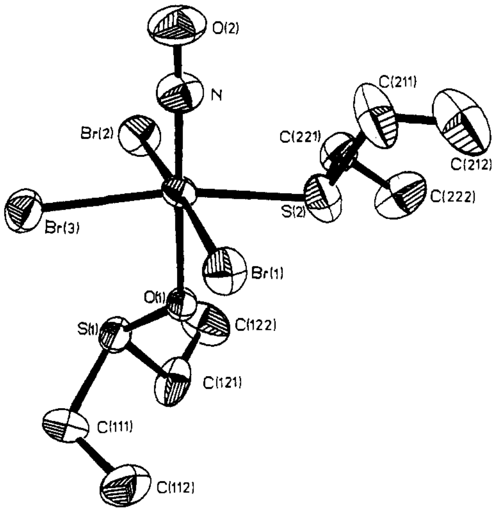

Figure 3. Perspective view of the tribromo(diethyl sulfide)(diethyl sulfoxide)nitrosylruthenium(II), $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$, molecule.

Crystal Structures. The two complexes $[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$ and $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$ have essentially octahedral coordination around the ruthenium atoms. Perspective views of the structures are given in Figures 2 and 3. In both compounds the molecules are well separated.

The three bromine atoms are in the meridonal arrangement in both complexes. In the complex $[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$ the two sulfides are trans to each other and the NO is trans to a bromine, whereas in $[Ru(NO)Br_3(Et_2S)(Et_2SO)]$ the sulfide and sulfoxide ligands are cis to each other and the NO is trans to the sulfoxide. The nitrosyl ligand is essentially linear with the Ru atom in both complexes. This, together with the length of the NO bond and the observed vibrational stretching frequencies (1847 and 1870 cm^{-1}) confirm that the NO is coordinated as NO^+. The Ru–NO and N–O bond lengths are typical of those found in other ruthenium nitrosyl compounds.[1,18-20]

The sulfoxide is clearly bonded to Ru through the oxygen atom, as found previously in the dimeric complex.[1] All of the Ru–Br

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(15) Page, C. T.; Fergusson, J. E. *Aust. J. Chem.* **1983**, *36*, 855.

(16) Evans, I. P.; Spencer, A.; Wilkinson, W. *J. Chem. Soc., Dalton Trans.* **1973**, 204.

(17) Mercer, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2480.

(18) Kimura, T.; Sakurai, T.; Shima, M.; Togano, T.; Mukaida, M.; Nomura, T. *Inorg. Chim. Acta* **1983**, *69*, 135.

(19) Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* **1978**, *17*, 2134.

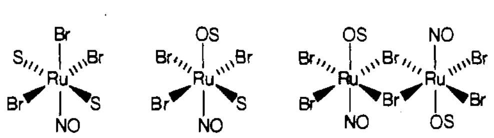
(20) Reed, J.; Soled, S. L.; Eisernberg, R. *Inorg. Chem.* **1974**, *13*, 3001.

Inorg. Chem. **1987**, *26*, 111-118

distances are around 2.5 Å, which is a typical value.[1,21-23] The Ru–Br bond trans to NO in [$Ru(NO)Br_3(n\text{-}Pr_2S)_2$] is not shortened, as is observed for the Ru–Cl bond in other nitrosyl chloro complexes.[24] The ν(NO) stretching frequency decreases in the order Cl > Br > I. The reason for the absence of Ru–Br bond shortening may be because of the difficulty of the larger Br atom getting close to the central metal atom. For the three complexes [$Ru(NO)Br_3(n\text{-}Pr_2S)_2$], [$Ru(NO)Br_3(Et_2S)(Et_2SO)$], and [$Ru(NO)Br_3(Et_2SO)$]$_2$, the distance of the approximately linear Br–Ru–Br system is relatively constant at 4.99, 5.01, and 5.01 Å respectively. The Ru–S and Ru–O bond lengths are typical of reported values.[1,17,19,20,23,25-27] As in the dimeric compound the S–O bond in [$Ru(NO)Br_3(Et_2S)(Et_2SO)$] of 1.543 (8) Å is similar to that found in other O-bonded sulfoxides. The S–O bond is shorter in S-bonded sulfoxides.[17,27]

The significant difference between the two complexes [$Ru(NO)Br_3(n\text{-}Pr_2S)_2$] and [$Ru(NO)Br_3(Et_2S)(Et_2SO)$] is that the two sulfides are trans to each other in the first compound and the sulfide and sulfoxide are cis in the second compound. The complex [$Ru(NO)Br_3(Et_2S)_2$] is expected to have the same stereochemistry as [$Ru(NO)Br_3(n\text{-}Pr_2S)_2$], based on an earlier ^{1}H NMR study.[2] Since the mixed sulfide/sulfoxide complex is derived from [$Ru(NO)Br_3(Et_2S)_2$], the difference in the arrangement of the sulfur-containing ligands in the two compounds may be due to the influence of the nitrosyl ligand. It is likely that the nitrosyl achieves better bonding (particularly Ru–NO π-back-bonding) when trans to oxygen than when trans to bromine. Unfortunately the disorder involving the NO ligand in [$Ru(NO)Br_3(n\text{-}Pr_2S)_2$] prevents one from obtaining an accurate Ru–N distance. Even so the Ru–N distance is longer (1.787 (9) Å) when NO is trans to the bromine in the bis(dipropyl)sulfide) complex than when it is trans to oxygen (1.72 (1) Å) in the sulfide/sulfoxide complex.

The stereochemical relationship between the two complexes whose structures have been determined and that of the dimer[1] is represented diagrammatically as follows:



It is suggested that the overall process is that one diethyl sulfide ligand is oxidized to sulfoxide, which then recoordinates trans to the NO. Then two molecules of the sulfide/sulfoxide complex condense together with elimination of Et_2S (and its oxidation to Et_2SO and Et_2SO_2) and production of the dimer.

Conclusion. The photochemical oxidation reaction of the complex [$Ru(NO)Br_3(Et_2S)_2$] requires radiation, dioxygen, and an electron donor (e.g. ethanol or sulfide). The reaction is considered as taking place in three steps. The first is the photochemical dissociation of some NO from the complex and the consequential oxidation of Ru(II) to Ru(III). An electron donor is also required in the reaction, but it does not depend on the presence of dioxygen. The second step is the oxidation of the sulfide, which requires both dioxygen and the liberated NO. Each reagent by itself does not achieve the oxidation. Radiation is unnecessary at this step, as is the electron donor. The third step is the condensation of two of the mixed sulfide/sulfoxide complexes to give the dimeric compound. The low solubility of the dimer and the continuing oxidation of the sulfide to sulfoxide and sulfone assists in this latter process.

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Registry No. $Ru(NO)Cl_3(i\text{-}Bu_2S)_2$, 105502-33-8; $Ru(NO)Br_3(n\text{-}PrPhS)_2$, 105502-34-9; $Ru(NO)Br_3(n\text{-}Bu_2S)_2$, 105502-35-0; $Ru(NO)Br_3(n\text{-}BuPhS)_2$, 105502-36-1; $Ru(NO)Br_3(i\text{-}Bu_2S)_2$, 105502-37-2; $Ru(NO)I_3(Et_2S)_2$, 105502-38-3; $Ru(NO)Br_3(Et_2S)(Et_2SO)$, 105502-39-4; [$Ru(NO)Cl_3(Et_2SO)$]$_2$, 105502-40-7; [$Ru(NO)I_3(Et_2SO)$]$_2$, 105502-41-8; $Ru(NO)Br_3(Me_2SO)_2$, 105517-96-2; $Ru(NO)Br_3(Et_2SO)_2$, 105517-97-3; $Ru(NO)Br_3(Et_2S)_2$, 61567-06-4; $Ru(NO)Br_3(n\text{-}Pr_2S)_2$, 61567-08-6; [$Ru(NO)Br_3(Et_2SO)$]$_2$, 59492-73-8; $Ru(NO)Cl_3(Me_2SO)_2$, 39734-03-7; $RuBr_3(NO)$, 68171-32-4; $RuBr_3(n\text{-}PrPhS)_3$, 32663-17-5; $RuBr_3(i\text{-}Bu_2S)_3$, 105502-42-9; Et_2S, 352-93-2; NO_2, 10102-44-0; $Ru(NO)Br_3(EtPhS)_2$, 61567-07-5; O_2, 7782-44-7.

Supplementary Material Available: Tables of root-mean-square amplitudes of vibration along the principal axes of their thermal ellipsoids for [$Ru(NO)Br_3(Et_2S)(Et_2SO)$], hydrogen atom coordinates and temperature factors and anisotropic thermal parameters of non-hydrogen atoms for [$Ru(NO)Br_3(n\text{-}Pr_2S)_2$], and additional bond angles for both compounds (5 pages); tables of observed and calculated structure factors for both compounds (19 pages). Ordering information is given on any current masthead page.

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(21) Collison, D.; Garner, C. D.; Mabbs, F. E.; King, T. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1820.

(22) Norwell, I. W.; Tabatabaian, K.; White, C. *J. Chem. Soc., Chem. Commun.* **1979**, 547.

(23) Oliver, J. D.; Riley, D. P. *Inorg. Chem.* **1984**, *23*, 156.

(24) Fergusson, J. E.; Rodley, G. A. *Inorganic Chemistry Series 2, Transition Metals Part 2*; Butterworths: London, 1975; p 71.

(25) Lai, T.-F.; Poon, C.-K. *J. Chem. Soc., Dalton Trans.* **1982**, 1465.

(26) Killops, S. D.; Knox, S. A. R.; Riding, G. H.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1978**, 486.

(27) Davies, A. R.; Einstein, F. W. B.; Farrell, N. P.; James, B. R. McMillan, R. S. *Inorg. Chem.* **1978**, *17*, 1965.

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Structural Isomers of the Rhenium Azobenzene Complex $CpRe(CO)_2(N_2Ph_2)$

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The azobenzene complexes $CpRe(CO)_2(N_2R_2)$ [**1**–**3**, Cp = η-C_5H_5; R = Ph (**1**), p-C_6H_4Me (**2**), p-C_6H_4F (**3**)] have been synthesized from $CpRe(CO)_2(THF)$ and the respective *trans*-azobenzene in hexane. The single-crystal X-ray structure determination for **1** reveals it to be isomer **1a** in which the azobenzene is bound "side-on" to the rhenium as η^2-*trans*-N_2Ph_2 with unequal Re–N bond lengths [Re–N(1) = 2.048 (12) Å, Re–N(2) = 2.136 (11) Å] and N(1)–N(2) = 1.415 (17) Å. The angle between the normals to the two N(1)–N(2)–C(phenyl) planes is 43°. Crystal data for **1a**: space group $P2_1$, $a = 8.3151$ (14) Å, $b = 11.2138$ (17) Å, $c = 9.5111$ (22) Å, $\beta = 105.75(2)°$, $V = 853.5$ Å^3, $Z = 2$, $d_{obsd} = 2.02$ (1) g cm^{-3}, $d_{calcd} = 1.905$ g cm^{-3}, $R_F = 0.0244$, $R_{wF} = 0.0271$. In solution, **1**–**3** each exist as two principal isomers, a and b, with distinguishable IR ν(CO) absorptions and ^{1}H NMR Cp resonances. These isomers are deduced to involve the azobenzene ligand bound in cyclic (η^2, a) and acyclic (η^1, b) forms, respectively. Analysis of the ^{1}H and ^{13}C NMR spectra, using variable-temperature and saturation-transfer experiments, indicates that the η^1-isomer (b) undergoes coordination site exchange between N(1) and N(2) and exchanges with the η^2-isomer (a) and that the η^2-isomer undergoes further fluxional behavior with a low activation barrier. This probably involves inversion at the nitrogen atoms.

Introduction

Part of the current work in our laboratory is directed at determining the structural, stereochemical, and chemical properties of complexes of molecules with unsaturated N–N moieties. These include complexes of dinitrogen (N_2), as well as diazenide (N_2H), diazene (HN═NH), and hydrazide (NNH_2 or $NHNH_2$), or their

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