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Figure 1. Infrared spectra of $[Ru(NH_3)_4Cl(SO_2)]Cl$ in the 1400–400-cm^{-1} region. From top to bottom these spectra are for the starting complex at 25 K, a sample photolyzed at 195 K, and a 25 K photolysis, respectively. Both photolyses are at 365 nm.

Photochemical Linkage Isomerization in Coordinated SO_2[1]

D. A. Johnson* and V. C. Dew

Sulfur dioxide (SO_2) is an extremely versatile ligand forming a variety of complexes, usually with low oxidation state metal ions.[2] The structural chemistry of complexes involving a direct metal–sulfur dioxide interaction is quite interesting with a number of well-established examples of the planar sulfur-bonded (i), pyramidal sulfur-bonded (ii), and η^2 (iii) structures shown below. Examples of oxygen-to-metal SO_2 coordination (iv) are not known for transition metals; however, this mode of coordination has been observed for the Lewis acid SbF_5.[3]
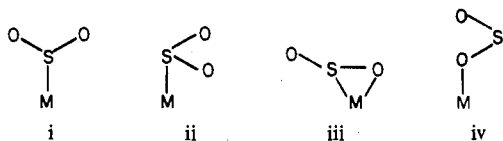
An analogy has been drawn between the metal–ligand stereochemical behavior of nitric oxide (NO) and sulfur dioxide (SO_2), and the importance of the energy match between the π^* molecular orbitals of these ligands and the nd orbitals of the metal ion in determining the stereochemistry of the interaction has been emphasized.[4,5] In this formalism, structures i and ii can be considered analogues of linear and bent nitrosyl ligands, respectively. In addition to the electronic relationship between NO and SO_2 noted above, sulfur dioxide is formally isoelectronic with NO_2^- and the isomeric interactions comparable to i, iii, and iv have been identified or postulated[6,7] analogues in the chemistry of the nitrite ligand. Thus, the stereochemistry of transition metal–SO_2 interactions is a mixture of parallels to the behavior of the ligands NO and NO_2^-.

Despite the many interaction modes for ligating SO_2, linkage isomers have not been observed.[8] We wish to report a previously undetected example of *photochemically induced* linkage isomerism in the solid-state photolysis of $[Ru(NH_3)_4Cl(SO_2)]Cl$ at 365 nm. The unstable linkage isomers of the SO_2
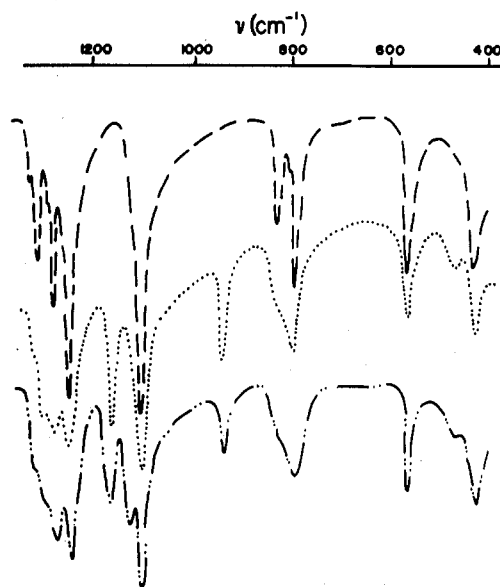
ligand produced in this photolysis can be trapped at low temperatures (25–195 K). The isomeric composition of the photoproduct can be altered by variation of the temperature of trapping and photolysis time, and infrared and electronic spectra indicate that more than one photoproduct is obtained in long photolyses at 25 K.

Experimental Section

The complex $[Ru(NH_3)_4Cl(SO_2)]Cl$ was prepared by the method of Wiberley et al.[9] Partial exchange of the sulfur dioxide oxygens was accomplished by dissolving the starting material in $H_2{}^{18}O–H_2{}^{16}O$ solution (pH > 3) which leads to hydration of the SO_2 to coordinated SO_3H^-.[10] The ^{18}O exchanged product was precipitated by bubbling with HCl (gas).

Infrared and electronic spectra were obtained in pressed KBr pellets (IR, UV-vis) and frozen HCl–H_2O glasses (visible) by using Perkin-Elmer 457 and Cary 14 spectrometers, respectively. Low-temperature spectra were measured by using a single-temperature cryostat of standard design and a variable-temperature Cryogenic Technology, Inc., Cryocooler.

Results

The starting complex has $\nu(SO)$ 1255 and 1110 cm^{-1} corresponding to the asymmetric and symmetric S–O stretching modes, respectively.[9] Photolysis of a KBr pellet of this complex at 195 K with 365-nm radiation causes a decrease in these bands and the production of new sulfur–oxygen absorptions at $\nu_I(SO)$ 1165 and $\nu_{II}(SO)$ 940 cm^{-1} (see Figure 1). The identification of these bands as $\nu(SO)$ is supported by preparation and photolysis of the deuterated and partially ^{18}O-exchanged samples of the starting material. Comparable infrared changes are observed for KBr pellets and Nujol mulls indicating that the photoreaction does not involve substitution by the matrix Br^- ions. The direction of the shifts in $\nu(SO)$ argues against formation of free SO_2, and the apparently low activation energy for the thermal reverse process suggests that substitution of the ammine ligands by lattice halide is unlikely. The infrared shifts suggest the photochemical conversion of the planar Ru(II)–SO_2 linkage of the starting material to either isomer ii or iii. The observed infrared changes are completely reversible at room temperature. Of the two suggested structures, the difference between the $\nu_I(SO)$ and $\nu_{II}(SO)$ (225 cm^{-1}) for the photoisomer is most consistent with the η^2 structure (iii). The infrared spectrum of the photolysis product of a partially ^{18}O-exchanged sample of $[Ru(NH_3)_4$-

Figure 2.

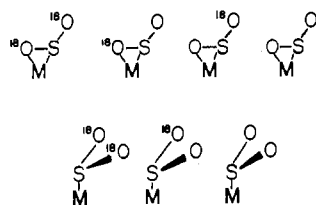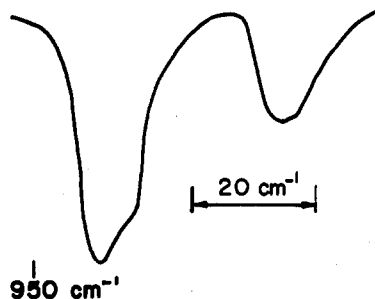**Figure 3.** Infrared spectrum in the 950-cm^{-1} region for a sample of [Ru(NH$_3$)$_4$Cl(SO$_2$)]Cl partially exchanged with ^{18}O labeled water. Sample was photolyzed at 195 K.

Table I. Infrared Absorptions (cm^{-1}) Associated with Ru^{II}-SO$_2$ Interaction

compd	ν_I(SO)	ν_{II}(SO)	δ(SO$_2$)
[Ru(NH$_3$)$_4$Cl(S^{16}O$_2$)]Cl	1255	1110	570
[Ru(ND$_3$)$_4$Cl(S^{16}O$_2$)]Cl	1270	1120	570
[Ru(NH$_3$)$_4$Cl(S^{16}O^{18}O)]Cl^a	1238	1085	560
[Ru(NH$_3$)$_4$Cl(S^{18}O$_2$)]Cl^a	1215	1065	550
[Ru(NH$_3$)$_4$Cl(η^2-SO$_2$)]Cl	1165	940	475
transient A^c	1180	b	b
transient C^d	1285	1130	560

^{a} Obtained from infrared spectrum of a mixture of ^{18}O isotopically labeled [Ru(NH$_3$)$_4$Cl(SO$_2$)]Cl. ^{b} Not observed, probable adsorption region obscured. ^{c} Short photolysis, T = 25 K, λ 365 nm (30–90 s). ^{d} Produced by photolysis of [Ru(NH$_3$)$_4$Cl-(η^2-SO$_2$)]Cl at 365 nm, T = 25 K.

Cl(SO$_2$)]Cl is also most consistent with a η^2 structure. For a sample having a mixture S^{16}O$_2$ and S^{16}O^{18}O ligands, three isotopically shifted ν(SO) bands for each mode are expected for a structure having equivalent S–O bonds but four bands would be observed if the S–O bonds are nonequivalent (see Figure 2). The ν_{II}(SO) band of the photoproduct for a partially ^{16}O/^{18}O exchanged product is shown in Figure 3. On the basis of the spectrum of the starting material (Table I) a symmetrical product would be expected to lead to three peaks with a total $\Delta\nu$ of ~40 cm^{-1}. The observed bands in the ~940-cm^{-1} region consist of two primary absorptions with additional partially resolved structure. We interpret this to indicate that ν_I(SO) and ν_{II}(SO) should be viewed as coupled ν(S=O) and ν(S—O) stretches of the free oxygen atom and metal-bonded oxygen atom of the η^2 structure, respectively. In this model, the ν_{II}(SO) vibration would primarily involve the motion of the oxygen bonded to the ruthenium atom and the 940- and 910-cm^{-1} absorption features of the photoisomer would involve complexes having ^{16}O or ^{18}O in this position. The smaller splitting would correspond to ^{16}O vs. ^{18}O substitution at the external oxygen. The combination of the difference between the frequencies of ν_I(SO) and ν_{II}(SO) for the S^{16}O$_2$ complex and the number of observed bands for the ^{16}O/^{18}O labeled mixture argue that the species which accumulates by photolysis at this temperature is the η^2 structure.

Photolyses at lower temperature (25 K) give evidence for additional isomeric species whose structures cannot be fully established at this time. During a short photolysis (30 s–2 min) at 25 K, an additional feature (A) at 1180 cm^{-1} is observed.
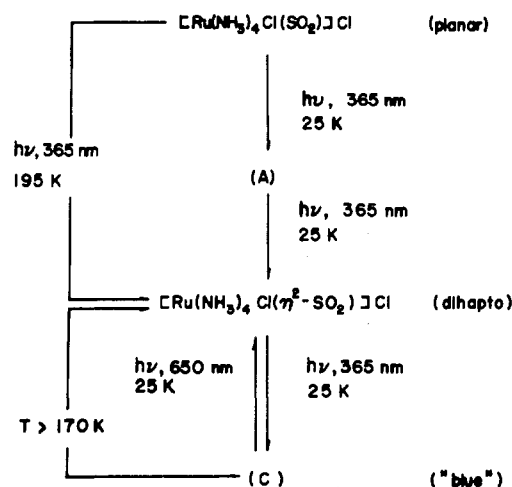
Figure 4. Postulated reaction scheme.

This absorption is overlapped by the 1160-cm^{-1} band of the η^2 structure for longer photolysis time. Other bands associated with this material have not been located. Prolonged photolysis of a sample at 25 K or *photolysis of a sample of the η^2 isomer produced at 195 K and brought to 25 K* leads to a third low-temperature species (C) with infrared bands at 1285, 1130, and 560 cm^{-1} (see Table I). Production of this species is accompanied by a color change from the red-brown of the starting material to a deep blue. The blue color of C is associated with a new electronic adsorption at 640 nm which disappears along with the new infrared bands by annealing at ca. 170 K. Similar color changes and absorption peaks are observed for photolysis of [Ru(NH$_3$)$_4$ClSO$_2$]Cl in HCl–H$_2$O glasses at 77 K. The disappearance of transient C at 170 K leads to production of the η^2 isomer. The η^2 transient can also be regenerated by photolysis of C in the 600–700-nm region at 25 K. The reaction scheme in Figure 4 summarizes observed thermal and photochemical changes. At this point the assignment of a probable structure to A and C must await for further experiments in progress. In particular, photolysis of isotopically substituted precursors which was helpful in defining the structure of the η^2 isomer is less informative due to overlapping absorption bands. The observed bands for species A and C would not be inconsistent with pyramidal and oxygen-bonded SO$_2$ isomers.

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