erage 90.0 [6]° and have a mean length of 2.010 [6] Å.[8] The axially coordinated oxygen atom of the dimethyl sulfoxide is essentially collinear, 177.0 (2)°, with the Pt–Pt bond at a bond distance of 2.126 (6) Å. In the sulfate groups the average S—O(coord) distance is 1.540 [5] Å, whereas the average S═O(terminal) bond length is 1.433 [12] Å. The difference, 0.107 [13] Å, is highly significant. Each sulfur atom is bent out of the O–Pt–Pt–O plane in the ring to which it belongs, and these bends are all in the same rotational sense about the Pt–Pt axis. Thus, while the central Pt_2O_8 unit has essentially D_{4h} symmetry, the entire $Pt_2(SO_4)_4$ unit has only C_{4h} symmetry. The structure of the central $Pt_2(SO_4)_4$ unit, with its C_{4h} symmetry, is very similar to what has been found previously in $Re_2(SO_4)_4$,[9] $Mo_2(SO_4)_4$,[10] $Mo_2(HPO_4)_4$,[11] and $Pt_2(HPO_4)_4$[5] moieties.

The Me_2SO ligand is coordinated through oxygen. While its dimensions are generally similar to those of free Me_2SO itself,[12] there is one striking difference, namely, the length of the S–O bond, which is now 1.554 (6) Å, as compared to 1.513 (5) Å in the uncoordinated molecule. This significant elongation, 0.041 (8) Å, is considerably greater than the very slight elongation, 0.012 (6) Å, observed in $Rh_2(O_2CCF_3)_4(Me_2SO)_2$.[13] This is not unexpected since the Pt atom in the present case is doubtless a more positively charged and less polarizable acceptor.

The potassium ions occupy a fourfold general position and have a coordination number of 8. Seven of the potassium ligators are oxygen atoms of the sulfate ions. Two of these, belonging also to the platinum coordination shell, make an average distance of 2.93 [1] Å to potassium, and the remaining five, peripheral sulfate oxgyen atoms, contact the potassium ion at an average distance of 2.79 [1] Å. One set of water molecules also serve as ligands to the potassium ions, with a K–O distance of 2.79 (1) Å. The second set of water molecules form hydrogen bonds to the first set, at an O···O distance of 2.86 (2) Å, and also to sulfate oxygen O(6), at a distance of 2.953 (8) Å. All of the K–O and O···O distances are available in a supplementary table.

Concluding Remarks. The Pt–Pt distance found here, 2.471 (1) Å, is not significantly different from that reported for the $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$ ion, 2.466 Å, with the assumption that the esd for the latter, which was not stated,[2] is 0.001 or 0.002 Å. While the Pt–Pt distance in the $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$ ion, 2.486 [2] Å,[5] is slightly lower in a statistically significant way, it is unlikely that the difference, 0.015 Å, has any chemical significance. The Pt–Pt bonds in these species with four bridging anions are distinctly shorter than those in the two compounds with only two bridging groups, viz., **2** and **3**, mentioned in the introduction, where the distances are respectively 2.557 (1) and 2.539 (1) Å.

Acknowledgment. We are grateful to the National Science Foundation for support.

Registry No. $K_2[Pt_2(SO_4)_4(OSMe_2)_2]\cdot 4H_2O$, 81602-75-7; $K_2[Pt_2(SO_4)_4(H_2O)_2]$, 58807-43-5.

Supplementary Material Available: Tables of structure factors, bond lengths and angles, thermal parameters, root-mean-square amplitudes, and noncovalent close contacts (Table IV) (17 pages). Ordering information is given on any current masthead page.

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(8) A number in parentheses is an esd for a given individual value while a number in brackets is equal to $[\sum \Delta_i^2/(n-1)]^{1/2}$, where Δ_i is the deviation of the *i*th value in a set of *n* such values from the arithmetic mean of the *n* values.

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Photoinduced Bimolecular Bidentate Ligand Migration. A New Photoinduced Reaction Pathway

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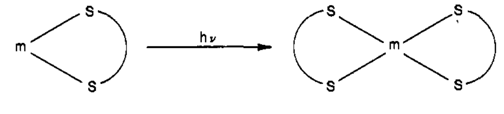
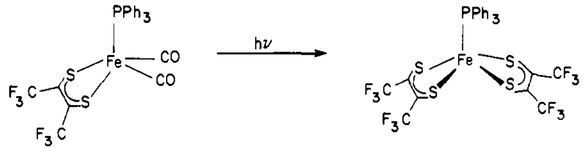
Received October 29, 1981

In the last decade there has been an upsurgence of interest in the photochemistry of inorganic and organometallic substances.[2-8] In this area, photoinitiated reactions of transition-metal carbonyl complexes are best characterized, but only a few generic reactions, namely, unimolecular ligand photosubstitution and intramolecular photorearrangement (isomerizations) have been well documented.[3] Herein, we describe a previously uncharacterized *photoinduced bimolecular bidentate ligand migration reaction*, eq 1, as observed for various 1,2-dithiolene complexes,[9] for example, eq 2.



(1)



(2)

1 **2**

Because of the inherent low symmetry and, consequently, uncharacterized electronic structure of **1** and **2**,[10] it was decided to find an alternative species that undergoes the same type photoreaction to serve as a model compound for the study of the reaction mechanism.

Careful study of the literature[11] revealed that the photogeneration of $M(CO)_n(S_2C_2R_2)_{3-n/2}$ (n = 0, 2, 4; M = W, Mo) from $M(CO)_6$ and $Ni(S_2C_2R_2)_2$ (R = CH_3, C_6H_5)[12] occurs (Scheme I). Assuming that it proceeds by the same mechanism as (2), we studied the photochemical transformation of $W(CO)_2(S_2C_2Me_2)_2$ (**3**) to $W(S_2C_2Me_2)_3$ (**4**) as a function of wavelength, solvent, and concentration. Herein we report our preliminary results.

Experimental Section

Authentic samples of trigonal-prismatic $W(CO)_2(S_2C_2(CH_3)_2)_2$[12] (red-violet; λ_{max} 641 (ϵ 850 M^{-1} cm^{-1}), 507 (15660), 347 nm (5520); ν_{CO} 2027, 1982 cm^{-1} ($CHCl_3$)) and $W(S_2C_2(CH_3)_2)_3$[13] (blue-green;

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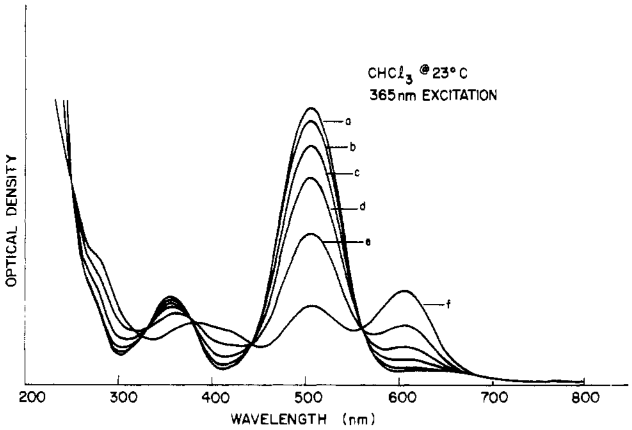
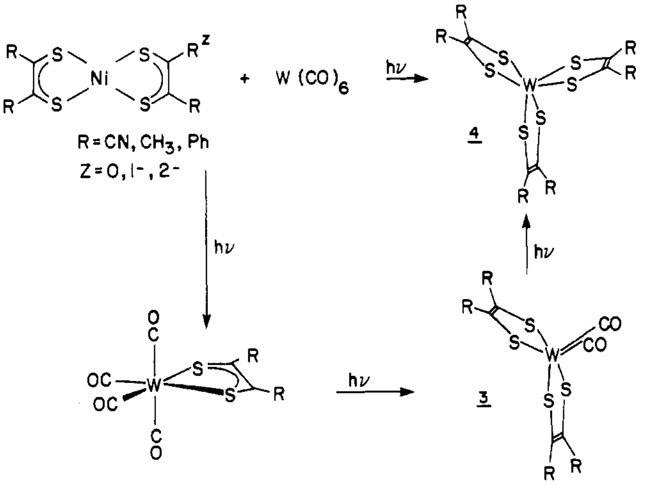


Figure 1. Absorption spectra of $W(CO)_2(S_2C_2Me_2)_2$ (trace a, 0.63 mM) as a function of irradiation with filtered 365-nm light in chloroform. Traces b–f refer to spectra taken at 2, 4, 9, 15, and 25 min.

Scheme I



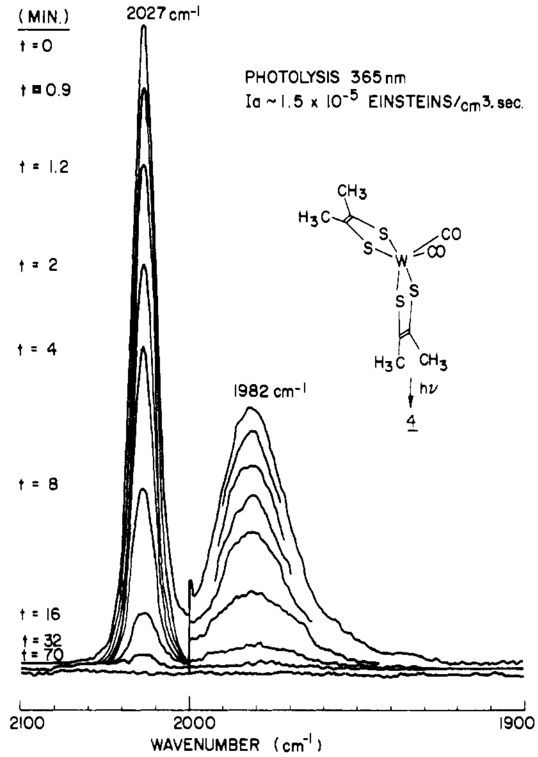


Figure 2. Infrared absorption spectra of $W(CO)_2(S_2C_2Me_2)_2$ as a function of 365-nm irradiation time in chloroform. The limiting spectrum shows no evidence for ν_{CO}; however, the presence of infrared spectral absorptions characteristic of $W(S_2C_2Me_2)_3$ was noted.

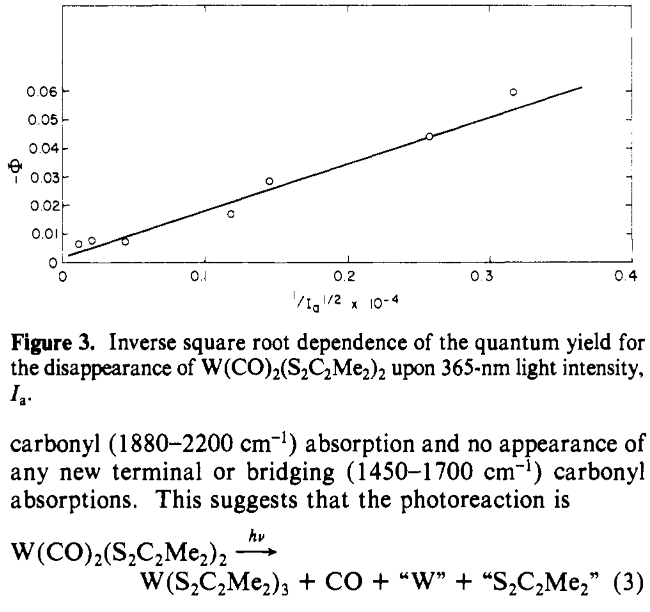


Figure 3. Inverse square root dependence of the quantum yield for the disappearance of $W(CO)_2(S_2C_2Me_2)_2$ upon 365-nm light intensity, I_a.

λ_{max} 770 (300), 608 (17950) 507 (4480), 405 nm (10250)) were prepared by methods found in the literature. Light intensity, I_a, was measured with a calibrated EG&G Model 450 radiometer/photometer. The absolute values of I_a are ±10%. Photolyses were carried out with a PEK Laboratories Model 911 lamp housing equipped with a Model 112 high-pressure Hg arc lamp operated at 100 W. Corning Glass band-pass filters were used to select irradiation wavelengths. Photolyses at 365-nm (27400 cm^{-1}) and 500-nm (20000 cm^{-1}) radiation were monitored with Cary 17D (UV–vis–near-IR) and Perkin-Elmer 283 infrared absorption spectrophotometers.

Results and Discussion

Photolysis of **3** for extended periods of time in chloroform[14] leads to the depletion of **3** and of the formation of **4** as evidenced from the UV–vis–near-IR spectra and comparisons with the spectra of authentic samples (Figure 1). Six isosbestic points are noted, and comparison of the spectra with those of authentic samples suggests that only two absorbing species are evident, i.e., **3** and **4**, in the 250–800 nm spectral region.[15] The possible formation of $W(CO)_6$ is ruled out by the failure to observe the characteristic ligand field absorption at 350 nm (ϵ ~1000 M^{-1} cm^{-1}) and ν_{CO} absorption at 1998 cm^{-1} (Figure 2). Photolysis of **3** with 365- or 500-nm radiation led to the complete disappearance of the terminal carbonyl (1880–2200 cm^{-1}) absorption and no appearance of any new terminal or bridging (1450–1700 cm^{-1}) carbonyl absorptions. This suggests that the photoreaction is

$$W(CO)_2(S_2C_2Me_2)_2 \xrightarrow{h\nu} W(S_2C_2Me_2)_3 + CO + \text{“W”} + \text{“}S_2C_2Me_2\text{”} \quad (3)$$

and tungsten plates out of the cuvette walls and does not occur in sufficient quantity to observe.

The quantum yield for the disappearance of **3** was 0.06 for irradiation at 365 nm and is approximately 100 times greater than the quantum yield for irradiation at 500 nm. Furthermore, the quantum yield exhibits an inverse square root dependency on light intensity, I_a (Figure 3).

This I_a dependence suggests that two photolytically generated radicals bimolecularly react to form the product, **4**, via a bidentate ligand transfer. A possible mechanism consistent with this data is CO loss by **3** to form $W(CO)(S_2C_2Me_2)_2$ followed by nucleophilic attack by a lone pair of sulfur electrons leading to a $W(S_2C_2Me_2)_2CO$ dimer, which rearranges to form the product, **4**, CO, "W", and the free ligand. The free ligand, $S_2C_2Me_2$, is unstable[16] and presumably decomposes

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(14) Similar results are obtained in benzene.

(15) At longer photolysis times small deviations from the isosbestic points occur in the UV. This is undoubtedly due to absorption of the photoproduced ligands and light scattered by W deposited on the cuvette walls.

to tetramethyl-1,4-dithiin. In the presence of acetone the photolysis of **3** does not lead to **4** and traps the dithiolene ligand and $(H_3C)_2C_2S_2C(CH_3)_2$ is presumably formed. A similar type of ligand exchange was thermally observed[17] for $M(S_2C_2(CN)_2)_2^-$ and $M(S_2C_2(CF_3)_2)_2^-$ (M = Cu, Ni, Pd).

Thus, we demonstrate the photoinduced bimolecular bidentate ligand migration reaction with the example of the 1,2-dithiolene ligand migration to a new metal center to form a photochemically stable perdithiolene complex.

Registry No. **3**, 12116-98-2; **4**, 12090-33-4.

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Evidence for Doublet-State Reactivity of the Tris(ethylenediamine)chromium(III) Ion in Aqueous Solution

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Received September 30, 1981

The identification of the ligand-field excited state(s) responsible for the photosubstitutional behavior of chromium(III) complexes has been a central and long-standing problem in inorganic photochemistry.[2,3] Early workers postulated that the doublet state, ^2E_g,[4,5] was photoreactive, but subsequent quenching and sensitization studies,[6–11] buttressed by theoretical models,[12–14] have provided some persuasive arguments that the lowest quartet excited state, $^4T_{2g}$, is the main or sole precursor to ligand labilization.[15]

A particularly contentious system has been $Cr(en)_3^{3+}$ (en is ethylenediamine). Irradiation into the lowest energy quartet absorption band ($^4A_{2g} \rightarrow {}^4T_{2g}$) of the complex in aqueous solutions causes both phosphorescent (doublet) emission and Cr–N bond cleavage (reaction 1).[16–18] Addition of various quenchers effects substantial quenching of the emission, whereas a smaller reduction in the reaction yield, ϕ, is observed.[10] While the unquenchable portion of the reaction must originate from directly formed $^4T_{2g}$, the quenchable component could result from (i) thermal repopulation of the reactive $^4T_{2g}$ state via back intersystem crossing from ^2E_g or (ii) direct reaction from ^2E_g.

$$Cr(en)_3^{3+} \xrightarrow[H^+]{h\nu} Cr(en)_2(en\text{-}H)OH_2^{4+} \qquad (1)$$

Detailed studies of the excited-state behavior of $Cr(en)_3^{3+}$ were undertaken in an attempt to assess the relative importance of these two pathways. On the basis of a kinetic analysis of quenching data, Ballardini et al.[10] concluded that *all* photochemistry originates from $^4T_{2g}$. The $^4T_{2g} \rightsquigarrow {}^2E_g$ and $^2E_g \rightsquigarrow {}^4T_{2g}$ intersystem crossing steps were assigned efficiencies of ~0.6 and ~1, respectively, so that essentially all of the excited molecules reaching ^2E_g ultimately return to $^4T_{2g}$ where reaction occurs (e.g., path i). Thus the chief role of the ^2E_g state is that of a temporary repository for excitation energy. Fukuda et al.[19] adopted the opposite view from a pulsed laser study of primary photoproduct formation. These workers concluded that the thermally equilibrated $^4T_{2g}$ state is formed directly with ~70% efficiency from the initially populated Franck–Condon state and then undergoes reaction 1 with a quantum yield of 0.17 ± 0.03; the thermally equilibrated ^2E_g state, on the other hand, is produced with ~30% efficiency via prompt intersystem crossing and subsequently reacts with a quantum yield of 0.8 ± 0.2 (e.g., path ii). Back intersystem crossing from ^2E_g to $^4T_{2g}$ was taken to be negligible.

A conceptually straightforward test for distinguishing between these alternative proposals involves direct irradiation into the doublet region of $Cr(en)_3^{3+}$. *Selective population* of ^2E_g would be expected to enhance the observed quantum yield for Cr–N bond breaking were path ii important but should leave ϕ essentially unchanged if path i dominates.[20] We report here the results of this doublet irradiation experiment.

Experimental Section

Commercially available (Alfa Inorganics) $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$ was twice recrystallized from concentrated perchloric acid solution. The resulting perchlorate salt was washed several times with absolute ethanol and dried over calcium sulfate in an evacuated desiccator. The electronic absorption spectrum of the complex in pH ~2.7 $HClO_4$ (maxima at 459 nm, $\epsilon = 76.0\ M^{-1}\ cm^{-1}$, and 350 nm, $\epsilon = 61.2\ M^{-1}\ cm^{-1}$) agrees closely with literature reports.[21] All spectral measurements were taken on a Cary 15 or 219 spectrophotometer.

Several light sources were used in the photochemical studies. Radiation centered at 404 nm with an 18-nm band width was provided by a 200-W high-pressure mercury-arc lamp in conjunction with interference and blocking filters. A CW Radiation 5-mW helium–neon laser was used for photolyses at 632.8 nm. Excitation at 669.2 nm with a power of 15–18 mW was accomplished with a Coherent Radiation Model 590 dye laser (containing Rhodamine B) pumped with a spectra Physics Model 164 argon ion laser; the output wavelength was determined to within ±0.2 nm by means of a Spex 1401 double monochromator.

Solutions of $Cr(en)_3^{3+}$ in pH 2.0–2.7 perchloric acid were irradiated in a 2-cm (404 nm) or a 20-cm (632.8 and 669.2 nm) jacketed cell. Temperature was maintained to ±0.2 °C by means of a circulating water bath or to ±0.8 °C by conducting the photolysis at ambient conditions in a constant-temperature darkroom. The contents of the cell were stirred periodically during irradiation to avoid bleaching of $Cr(en)_3^{3+}$ in the light beam. The extent of reaction 1 (generally

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