3810 *Inorg. Chem.* **1992,** *31,* 3810–3817

Disproportionation of SO_2 to S_8 and SO_3 on $Cp^*{}_2Cr_2S_5$. Crystallographic and ^{34}S-Labeling Evidence for an Oxygen-Transfer Mechanism and Observation of Facile Exchange of Cr_2S_5 Core Sulfurs with ^{34}S. Structures of $Cp^*{}_2Cr_2(\mu\text{-}S)(\mu\text{-}\eta^2\text{-}S_2)(\mu\text{-}\eta^1\text{-}SS{\cdot}SO_2){\cdot}SO_2$ and $Cp^*{}_2Cr_2(\mu\text{-}S)(\mu\text{-}\eta^2\text{-}S_2)(\mu\text{-}SSO_3)$

Andreas Toupadakis, Gregory J. Kubas,* and Carol J. Burns

Inorganic and Structural Chemistry Group (INC-1), MS-C346, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545

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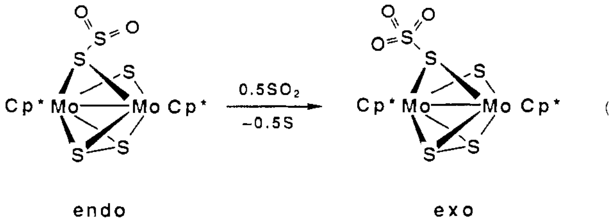
The syntheses, structures, and reactivities of $Cp^*{}_2Cr_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SS{\cdot}SO_2){\cdot}SO_2$, **1**·$2SO_2$, and $Cp^*{}_2Cr_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SSO_3){\cdot}(CD_3OD)_{lattice}$, **2**, are reported. Reversible addition of SO_2 to $Cp^*{}_2Cr_2S_5$, **1**, to give **1**·$2SO_2$ was found to occur at room temperature. **1** possesses a novel $\mu\text{-}\eta^1\text{-}S_2$ ligand, and X-ray crystallography of **1**·$2SO_2$ showed that SO_2 binds as a Lewis acid to the terminal sulfur of this ligand with an acute S–S–S angle (94°). The S–SO_2 distance of 2.41 Å is about 0.2 Å shorter than in the previously known $Cp^*{}_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}S{\cdot}SO_2)$. Consistent with this greater activation, **1**·$2SO_2$ further reacts in the presence of excess SO_2 to give the thiosulfate **2** (isomorphous to the Mo analogue) at a *much faster rate* than in the Mo system. Significantly, the crystal structure of **1**·$2SO_2$ shows the presence of associated SO_2 molecules unsymmetrically bridging (via sulfur) the oxygen atoms of each sulfide-bound SO_2 molecule to give a cyclic aggregate of four SO_2 molecules (intermolecular S···O distances of 2.78 and 2.95 Å). Infrared studies demonstrate that these interactions further activate (weaken) the S=O bonds of the sulfide-bound SO_2. Thus, it is proposed that the mechanism of SO_2 disproportionation in solution involves base-assisted oxygen atom transfer from the sulfide-bound SO_2 molecule to the associated SO_2 to produce SO_3. The SO_3 then displaces S_2O (which decomposes to S_8 and SO_2) from the bridging sulfide ligand to give the observed thiosulfate product. The reactivities of **1**·$2SO_2$ and $Cp^*{}_2Cr_2S_4{\cdot}SO_2$ vs $Cp^*{}_2Mo_2S_4{\cdot}SO_2$ and of **2** vs $Cp^*{}_2Mo_2S_4{\cdot}SO_3$ are discussed. A mechanism for the oxygen atom transfer reaction is proposed on the basis of the crystal structure of **1**·$2SO_2$ and ^{34}S-labeling studies. Facile reaction of $Cp^*{}_2Cr_2S_4$ with S_8 was found to give **1**, and all *five* of the core sulfurs in the latter incorporated ^{34}S if excess $^{34}S_8$ was used. **1**·$2SO_2$ and **2** crystallize in the space groups $C2/c$ and $P\bar{1}$, respectively. The cell dimensions are the following: **1**·$2SO_2$, a = 16.087 (4) Å, b = 15.926 (3) Å, c = 21.650 (3) Å, β = 105.29 (2)°, and Z = 8; **2**, a = 10.336 (2) Å, b = 10.891 (2) Å, c = 13.219 (3) Å, α = 85.15 (3)°, β = 78.85 (3)°, γ = 62.39 (3)°, and Z = 2. R = 4.85% for **1**·$2SO_2$, and R = 4.84% for **2**.

Introduction

Although transition-metal-mediated transfer of oxygen atoms to SO_2 from O_2 or other sources to generally give sulfate-containing species is quite common, only a few examples are known of O atom transfer *between* two or more SO_2 molecules on metal complexes.[1,2] The simple disproportionation reaction[3] $2SO_2 \rightarrow SO_3 + SO$ is complicated by the instability of SO, which instantly disproportionates to S_8 and SO_2, and the strong oxidizing ability of SO_3. Thus, potential catalysts for SO_2 breakdown must resist sulfur poisoning and oxidation. Stoichiometric disproportionation of SO_2 has recently been found in three diverse reaction systems: $Cp^*Ru(CO)_2H$,[1b] $Mo(N_2)_2(dppe)_2$,[1c] and $Cp^*{}_2Mo_2S_4$.[2] In all cases free SO_3 is not formed but is tied up by bases (μ-S to give the μ-SSO_3 ligand[1b,2]) or inserts into the Ru–H bond.[1b] Free sulfur[2] or sulfido ligands[1b,c] are the coproducts. Such disproportionation processes may indeed be a hidden mechanistic feature of many SO_2 reactions, and reduction of $S^{IV}O_2$ may actually go through $S^{VI}O_3$-containing intermediates from SO_2 disproportionation. In this regard we have reported[4] that catalytic conversion of SO_2 to exclusively S_8 and H_2O is achievable using $Cp^*{}_2Mo_2S_4$ as a sulfur-resistant catalyst and hydrogen as a reductant (eq 1, Figure 1). Reaction of SO_2 with solutions of

$$SO_2 + 2H_2 \rightarrow {}^1\!/_8S_8 + 2H_2O \qquad (1)$$

$Cp^*{}_2Mo_2S_4$ initially yields the adduct $Cp^*{}_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}S{\cdot}SO_2)$, which was shown by crystallography to contain an SO_2 molecule weakly bound to a μ-S ligand as the endo isomer (S–S = 2.60 Å).[2] This adduct further reacts with SO_2 (eq 2) to quantitatively give $Cp^*{}_2Mo_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SSO_3)$, which now contains an SO_3 fragment bound to the μ-S in exo fashion and can be regarded as a thiosulfate complex (S–S = 2.17 Å).



(2)

The SO_3 fragment is formed by an oxygen atom transfer process, and as established by ^{18}O labeling, *the source of the oxygen is* SO_2. Sulfur is also produced in eq 2, showing that SO_2 has

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(1) (a) Moody, D. C.; Ryan, R. R. *J. Chem. Soc., Chem. Commun.* **1980**, 1230. (b) Kubat-Martin, K. A.; Kubas, G. J.; Ryan, R. R. *Organometallics* **1989**, *8*, 1910. (c) Lorenz, I.-P.; Walter, G.; Hiller, W. *Chem. Ber.* **1989**, *123*, 979.

(2) Kubas, G. J.; Ryan, R. R.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1989**, *111*, 7823.

(3) The reaction of concern here is metal-mediated oxygen *atom* transfer and not the concept of self-ionization equilibrium, i.e., $2SO_2 \rightleftharpoons SO_3{}^{2-} + SO^{2+}$ (Jander, G. *Die Chemie in Wasserahnlichen Losungsmitteln*; Springer-Verlag: Berlin, 1949; pp 209–307). Also, related "oxide ion" transfers such as that reported in isotopic exchange reactions of liquid SO_2 and SO_3 (Huston, J. L. *J. Am. Chem. Soc.* **1951**, *73*, 3049) are unlikely to occur in the chemistry here.

(4) Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 6138.

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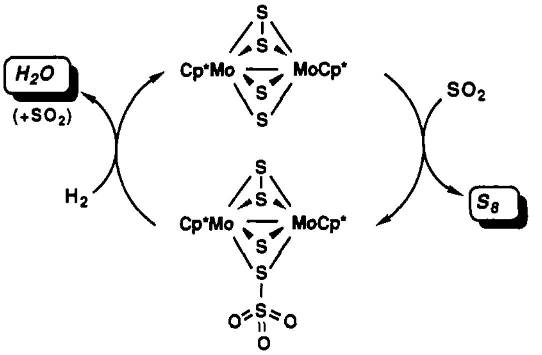

Figure 1. Catalytic reduction of SO_2 to S_8 and H_2O, using the complex $Cp_2{}^*Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ as catalyst, and hydrogen as reductant.

effectively undergone net disproportionation to SO_3 and S_8. The thiosulfate is readily hydrogenated at 25–75 °C to regenerate $Cp^*_2Mo_2S_4$ with concomitant formation of H_2O and SO_2 (eq 3), completing the proposed catalytic cycle for eq 1 (Figure 1).

$$Cp^*_2Mo_2S_4{\cdot}SO_3 + H_2 \rightarrow SO_2 + H_2O + Cp^*_2Mo_2S_4 \qquad (3)$$

We report here that similar chromium sulfide complexes such as $Cp^*_2Cr_2S_5$, **1**, originally prepared by Wachter[5,6] are even *more active* than the molybdenum sulfides in cleaving SO_2. The $Cr/S/SO_2$ chemistry has led to the structural characterization of two complexes, the very revealing biactivated SO_2 adduct $Cp^*_2Cr_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SS{\cdot}SO_2){\cdot}SO_2$, **1**·$2SO_2$, and the "$SO_3$ adduct" $Cp^*_2Cr_2S_4{\cdot}SO_3$, **2**, which importantly now contains one less sulfur and is isostructural with the Mo species discussed above. The crystal structure of **1**·$2SO_2$ as well as ^{34}S-labeling studies suggest a possible oxygen-transfer mechanism for the conversion of **1**·$2SO_2$ to **2** in which *self-aggregation of SO_2 via weak Lewis acid–base interactions induced by electron donation from sulfide* plays a critical role.

Experimental Section

Reactions were carried out under inert atmosphere using Schlenk techniques. Reagent grade solvents and SO_2 were usually used as received, but for some reactions solvents were dried by distillation from appropriate drying agents. ^{34}S was obtained from the Mound Facility of Monsanto Research Corp., Miamisburg, OH. Samples of $Cp^*_2Cr_2S_4$, $Cp^*_2Cr_2S_5$, and $Cp'_2W_2S_4$ (Cp' = *t*-BuCp) were generously provided by Professor J. Wachter of the University of Regensburg, and the Cr species[5,6] were also prepared by modification of literature methods. FT-IR and ^1H NMR spectra were recorded on Biorad FTS-40 and Brucker AM-200 instruments, respectively. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Mass spectroscopy (electron impact ionization) was carried out by Oneida Research Services, Inc., Whitesboro, NY.

Synthesis of 1·$2SO_2$. The green solid **1** (0.20 g) was dissolved in dry degassed toluene, and a green solution was obtained. When SO_2 was passed through the solution, the color changed at once to brown-yellow. Heptane, which was degassed with SO_2, was added to the brown-yellow solution, and the product precipitated as a microcrystalline solid in a quantitative yield. The complex was collected on a frit, washed with SO_2-saturated heptane, and dried in a stream of SO_2 gas. The SO_2 interacting with the sulfide-coordinated SO_2 of **1**·$2SO_2$ is readily lost if exposed to air or if an SO_2-enriched atmosphere is not maintained over the complex. The sulfide-bound SO_2 is more tightly held but readily dissociates in solution under vacuum.

Synthesis of $Cp^*_2Cr_2S_4{\cdot}SO_3$, 2. Method A. From Pure 1. **1** (0.12 g) was dissolved in dry degassed PhCl (3 mL), and the characteristic olive green solution was obtained. When SO_2 was passed through the solution, the color changed at once to brown-yellow. Next methanol (1 mL, degassed with SO_2) was added, and the solution turned to bright green in about 15 min. The green solution was stirred for an additional 30 min, and then full vacuum was applied for 10 min. When a solid started to form, heptane was added and the product precipitated as a green microcrystalline solid in quantitative yield. It was filtered, washed with heptane, and dried under vacuum. The complex is stable in air in the solid or solution states. Anal. Calcd for $C_{20}H_{30}O_3Cr_2S_5$: C, 41.22; H, 5.19; S, 27.51. Found: C, 41.00; H, 4.91; S, 27.34.

The above reaction can also be carried in toluene containing ~1% Et_3N (10 min) or liquid SO_2 (30 min).

Method B. From Crude 1. The procedure[5b] for the preparation of **1** was followed, using ~2 g of $[Cp^*Cr(CO)_2]_2$ starting material. Instead of chromatographic separation, the toluene solution of crude product obtained was reduced in volume by ~50% in vacuo, filtered, and treated with excess SO_2 for 30 min to form primarily the adduct **1**·$2SO_2$. Addition of heptane and storage in a refrigerator overnight precipitated selectively only the crystalline SO_2 adduct and a small amount of bright green **2**. This was then dissolved in a minimum amount of toluene, an equal volume of MeOH was added, and the solution was stirred under SO_2 for 30 min. The bright green solution, which was found to contain exclusively **2** by NMR, was reduced in volume, treated with heptane after precipitation first began, and allowed to stand to complete precipitation. The resulting green solid was collected, washed with CS_2 to remove any residual elemental sulfur, and dried in vacuo; NMR confirmed it to be pure **2**, in yield approximately equivalent to that reported for the synthesis[5b] of **1** (14–17%).

Reactions of $Cp^*_2Cr_2S_4$ with Sulfur To Form $Cp^*_2Cr_2S_5$, 1. Preparation of ^{34}S-Labeled 1. A green-blue solution of $Cp^*_2Cr_2S_4$ in $CDCl_3$ in an NMR tube showed a strong Cp* ^1H resonance at 1.96 ppm plus a minor signal at 1.91 ppm possibly due to an isomeric form or impurity. Upon addition of excess S_8, the solution immediately turned green-yellow and NMR showed that a new sharp singlet appeared at 2.14 ppm due to **1**. Only a very weak peak remained at 1.96 ppm. Similar results were obtained in toluene-d_8 solution, wherein the respective NMR signals shifted from 1.83 (major) and 1.78 ppm (minor) to 1.98 ppm characteristic of the S_5 species.

In order to attempt to prepare $Cp^*_2Cr_2S_4{}^{34}S$ specifically labeled at the terminal sulfur of the η^1-S_2 ligand, $Cp^*_2Cr_2S_4$ (15 mg, 0.030 mmol) in 10 mL of $CHCl_3$ was reacted with 4 mg of $^{34}S_8$ (0.015 mmol, 4-fold excess). After 10 min, the solution was filtered to remove unreacted sulfur, and solvent was slowly removed from the filtrate in vacuo over about a 3-h period. NMR of the solid residue showed that the expected **1** had formed (δ_{Cp^*} = 2.13 ppm) plus a trace of **2** (probably a carry-over impurity of $Cp^*_2Cr_2S_4$). Mass spectroscopic studies showed that complete isotopic scrambling of the core sulfurs occurred. Although only very weak parent ion peaks of **1** were observed by either chemical ionization or electron impact, the fragments from loss of one or more sulfurs were readily seen to give masses due to complete isotopomeric sets (see Results and Discussion). Electron impact methods were found to give generally better spectra.

Preparation of ^{34}S-Labeled 1·$2SO_2$ and Its Oxygen-Transfer Reaction with SO_2. $Cp^*_2Cr_2S_4$ (20 mg, 0.040 mmol) and $^{34}S_8$ (6 mg, 0.022 mmol) were stirred in 3 mL of toluene containing ca. 1 mL of $CHCl_3$ (to aid solubility). After several hours of equilibration, during which some solids (mostly sulfur) remained undissolved, the green solution was filtered and treated with SO_2. SO_2-saturated heptane was added to the now brown solution, which was placed in a refrigerator overnight for crystallization. The mixture was decanted, and the brown crystalline SO_2 adduct was washed three times with CS_2 containing SO_2 to remove any traces of sulfur (which would interfere with mass spectroscopic analysis of the products of subsequent reaction with SO_2).

A sample of the above adduct was dissolved in a minimum amount of $CHCl_3$ under SO_2 and MeOH added. The characteristic bright green color of **2** was obtained, and all volatiles were removed in an SO_2 stream. The residue was then used for mass spectroscopic and IR analysis of the isotopic compositions of the **2** and S_8 products.

X-ray Crystallography of 1·$2SO_2$. A dark brown-red prismatic crystal of **1**·$2SO_2$ was fixed in Apiezon grease on a glass fiber and transferred directly to the cold stream (−70 °C) of a Siemens diffractometer. The data collection and results are summarized in Table I. The structure was partially solved from direct methods and then solved and refined using Fourier difference maps. Tables of further details of the crystallography, atomic coordinates, and anisotropic thermal parameters are given as supplementary material.

X-ray Crystallography of $Cp^*_2Cr_2S_4{\cdot}SO_3{\cdot}(CD_3OD)_{lattice}$. A large crystal was cleaved in half to give a dark-green pyramidal crystal, which

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(5) (a) Brunner, H.; Wachter, J.; Guggolz, E.; Ziegler, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 1765. (b) Wachter, J.; Brunner, H.; Meier, W. *Inorg. Synth.* **1990**, *27*, 69.

(6) (a) Brunner, H.; Kauermann, H.; Meier, W.; Wachter, J. *J. Organomet. Chem.* **1984**, *263*, 183. (b) Brunner, H.; Pfauntsch, J.; Wachter, J.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1989**, *359*, 179.

Table I. Crystallographic Data for **1**·2SO$_2$ and **2**-CD$_3$OD

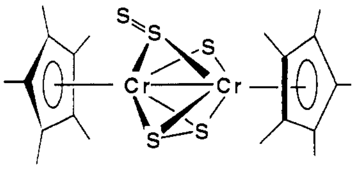
	1·2SO$_2$	**2**·CD$_3$OD
chem formula	$C_{20}H_{30}Cr_2O_4S_7$	$C_{21}H_{34}Cr_2O_4S_5$
a, Å	16.087 (4)	10.336 (2)
b, Å	15.926 (3)	10.891 (2)
c, Å	21.650 (3)	13.219 (3)
α, deg		85.15 (3)
β, deg	105.29 (2)	78.85 (3)
γ, deg		62.39 (3)
V, Å^3	5350 (2)	1293.7 (5)
Z	8	2
fw	662.9	614.8
space group	$C2/c$	$P\bar{1}$
T, °C	−70	25
λ, Å	0.710 73	0.710 73
ρ_{calcd}, g·cm^{-3}	1.646	1.578
μ, cm^{-1}	13.45	12.34
R^a	0.048	0.048
$R_w{}^b$	0.049^c	0.085^d

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$. [c] $w = [\sigma^2(F_o) + 0.0002F_o{}^2]^{-1}$. [d] $w = [\sigma^2(F_o) + 0.0016F_o{}^2]^{-1}$.

was encased in epoxy cement and transferred to an Enraf-Nonius diffractometer at room temperature. The data collection and results are summarized in Table I. The hydrogen positions were calculated and fit by a riding model. Tables of further details of the crystallography, atomic coordinates, and anisotropic thermal parameters are given as supplementary material.

Results and Discussion

SO$_2$ Binding to Sulfide Ligands of Cp*$_2$Cr$_2$S$_5$ and Cp*$_2$Cr$_2$S$_4$. The novel complex characterized by Wachter, Cp*$_2$Cr$_2$S$_5$, **1**, contains both an η^2-S$_2$ and a rare η^1-S$_2$ ligand bridging the metal centers.[5] It was found that reversible addition of SO$_2$ to this complex occurs at room temperature. A green solution of **1** in toluene changes immediately to a brown-yellow color upon the addition of SO$_2$ gas, and when vacuum is applied, the green color is obtained again. Addition of SO$_2$-saturated heptane to the brown-yellow toluene solution quantitatively produces the new complex **1**·2SO$_2$ as a dark solid. The IR of crystals of the latter obtained by slow cooling shows bands for *two* kinds of SO$_2$ molecules, with one set of frequencies at 1197 and 1056 cm^{-1} and the other at 1318 and 1144 cm^{-1}. Compared to band positions for coordinated[7] SO$_2$ and free SO$_2$ (1361 and 1151 cm^{-1} in the gas phase[8]), the lower-energy set is consistent with SO$_2$ bound to a metal or ligand as a Lewis acid.



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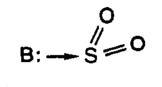


The bands at much higher frequency are most probably due to weakly associated SO$_2$ (coordination to the metal as a Lewis base, which could also give high ν_{SO}, is unlikely here because of the reversibility of the binding and electronic considerations[7]). Obviously, both types of SO$_2$ are activated, with the coordinated one more activated than the associated molecule because the lowering of ν_{SO} can be qualitatively correlated with the strength of the Lewis base B to which SO$_2$ is bound. When the Nujol mull sample is left to stand, SO$_2$ slowly escapes, and the bands due to associated SO$_2$ diminish. Eventually only the bands of the coordinated SO$_2$ remain but are *shifted to higher energy*, i.e., 1209 and 1063 cm^{-1}. This demonstrates that there is an *interaction* between the two kinds of SO$_2$ molecules, which is in accord with the X-ray crystallographic results obtained on this complex given below.

Table II. Nujol Mull IR and ^{1}H NMR (Cp*) Data for Cr and Mo Sulfide Complexes

complex	ν_{SO}, δ_{SO}, cm^{-1}	$\delta_{MeOH\text{-}d_4}$	δ_{CDCl_3}	$\delta_{toluene\text{-}d_8}$
Cp*$_2$Cr$_2$S$_5$			2.14^a	1.98
Cp*$_2$Cr$_2$S$_5$·SO$_2$·(SO$_2$)	1197, 1056, 523 1318, 1144, 527		2.14	
Cp*$_2$Cr$_2$S$_4$		1.95,^{b} 1.88^c	1.96,^{b}, 1.91^c	1.83,^{b} 1.78^c
Cp*$_2$Cr$_2$S$_4$·SO$_2$			2.15	1.88,^{b} 1.86^c
Cp*$_2$Cr$_2$S$_4$·SO$_3$	1228, 1204, 1012, 610^d	2.23	2.24^d	1.93
Cp*$_2$Mo$_2$S$_4$			2.14^e	
Cp*$_2$Mo$_2$S$_4$·SO$_2$	1229, 1080, 533^e		2.13^e	
Cp*$_2$Mo$_2$S$_4$·SO$_3$	1242, 1205, 1010, 604^e		2.31^e	

[a] Lit.[5] δ_{CDCl_3} = 2.13 ppm. [b] Major peak (lit.[6a] δ_{CDCl_3} = 1.98 ppm). [c] Minor peak. [d] Lit[6b] ν_{SO} = 1229, 1207, 1010, 600; δ_{CDCl_3} = 2.24 ppm. [e] Reference 2.

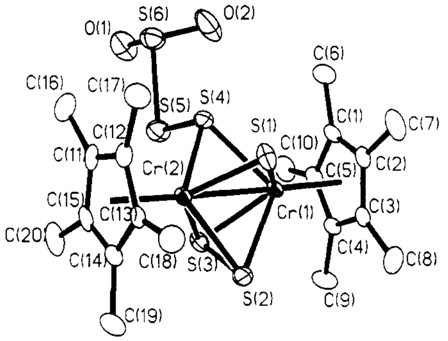
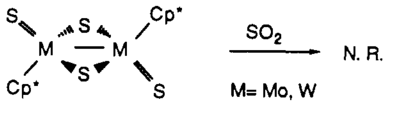


Figure 2. ORTEP drawing (50% ellipsoids) of the structure of **1**·2SO$_2$, shown without associated SO$_2$ molecules.

The S$_4$ complex Cp*$_2$Cr$_2$S$_4$, which can be prepared by abstraction of the terminal sulfur from **1** by PPh$_3$, has a (μ-η^2-S$_2$)(μ-S)$_2$ structure similar to the Mo analogue.[6] Addition of SO$_2$ to CDCl$_3$ or toluene-d_8 solutions of this complex in NMR tubes showed color changes from deep green-blue to olive green and relatively large shifts (0.05–0.19 ppm) in the Cp* NMR signals compared to the Mo analogue or **1** (Table II).

The tungsten analogue Cp*$_2$W$_2$(μ-S$_2$)(μ-S)$_2$ is unknown, and its reactivity toward SO$_2$ could not be compared to those of the Cr and Mo complexes. However, no reaction of SO$_2$ with the isomeric species containing terminal sulfides, Cp′$_2$W$_2$(S)$_2$(μ-S)$_2$ (Cp′ = t-BuCp), was observed, as also had been the case for the Cp*Mo analogue.[2]



Clearly not every sulfide complex will bind or activate SO$_2$, and the rationale for this awaits more comprehensive studies.

X-ray Structure of 1·2SO$_2$. Crystals of **1**·2SO$_2$ were grown from concentrated toluene solutions, carefully layered with SO$_2$-saturated heptane overnight at 10 °C, and the structure of **1**·2SO$_2$ was determined from diffraction data collected at −70 °C. The molecular structure (Figure 2) shows SO$_2$ binding to the novel μ-η^1-S$_2$ ligand (S–SO$_2$ = 2.41 Å) with an acute 94° S–S–S angle (bond distances and angles are given in Table III). Most interestingly, the structure also shows that the oxygen atoms of each coordinated SO$_2$ molecule interact with the sulfur atoms of two associated SO$_2$ molecules to form an eight-membered ring (Figure 3). The ring is nearly planar, with a mean deviation from the least-squares plane of 0.147 Å (Figure 4). The S–O distances are unequal (2.776 and 2.954 Å), both of which are

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(7) Kubas, G. J. *Inorg. Chem.* **1979**, *18*, 182.
(8) Grigg, E. C. M.; Johnston, G. R. *Aust. J. Chem.* **1966**, *19*, 1147.

Table III. Bond Lengths (Å) and Angles (deg) for **1**·$2SO_2$

	Bond Lengths		
Cr(1)–Cr(2)	2.497 (6)	Cr(1)–S(1)	2.227 (10)
Cr(1)–S(2)	2.319 (9)	Cr(1)–S(3)	2.332 (9)
Cr(1)–S(4)	2.358 (9)	Cr(1)–C(1)	2.235 (30)
Cr(1)–C(2)	2.234 (30)	Cr(1)–C(3)	2.220 (28)
Cr(1)–C(4)	2.211 (26)	Cr(1)–C(5)	2.218 (31)
Cr(2)–S(1)	2.224 (10)	Cr(2)–S(2)	2.326 (8)
Cr(2)–S(3)	2.341 (9)	Cr(2)–S(4)	2.339 (10)
Cr(2)–C(11)	2.239 (28)	Cr(2)–C(12)	2.221 (27)
Cr(2)–C(13)	2.214 (30)	Cr(2)–C(14)	2.222 (30)
Cr(2)–C(15)	2.234 (30)	S(2)–S(3)	2.027 (13)
S(4)–S(5)	2.085 (14)	S(5)–S(6)	2.414 (13)
S(6)–O(1)	1.449 (32)	S(6)–O(2)	1.456 (26)
S(7)–O(3)	1.400 (33)	S(7)–O(4)	1.409 (34)
	Bond Angles		
Cr(2)–Cr(1)–S(1)	55.8 (3)	Cr(2)–Cr(1)–S(2)	57.6 (2)
S(1)–Cr(1)–S(2)	83.9 (3)	Cr(2)–Cr(1)–S(3)	57.9 (2)
S(1)–Cr(1)–S(3)	112.8 (3)	S(2)–Cr(1)–S(3)	51.7 (3)
Cr(2)–Cr(1)–S(4)	57.5 (2)	S(1)–Cr(1)–S(4)	75.4 (3)
S(2)–Cr(1)–S(4)	112.4 (3)	S(3)–Cr(1)–S(4)	79.1 (3)
		Cr(1)–Cr(2)–S(1)	55.9 (3)
Cr(1)–Cr(2)–S(2)	57.4 (2)	S(1)–Cr(2)–S(2)	83.8 (3)
Cr(1)–Cr(2)–S(3)	57.5 (2)	S(1)–Cr(2)–S(3)	112.5 (3)
S(2)–Cr(2)–S(3)	51.5 (3)	Cr(1)–Cr(2)–S(4)	58.3 (7)
S(1)–Cr(2)–S(4)	75.9 (3)	S(2)–Cr(2)–S(4)	112.8 (3)
S(3)–Cr(2)–S(4)	79.3 (3)		
Cr(1)–S(1)–Cr(2)	68.3 (3)	Cr(1)–S(2)–Cr(2)	65.0 (3)
Cr(1)–S(2)–S(3)	64.5 (4)	Cr(2)–S(2)–S(3)	64.7 (3)
Cr(1)–S(3)–Cr(2)	64.6 (3)	Cr(1)–S(3)–S(2)	63.8 (4)
Cr(2)–S(3)–S(2)	63.9 (3)	Cr(1)–S(4)–Cr(2)	64.2 (3)
Cr(1)–S(4)–S(5)	111.9 (4)	Cr(2)–S(4)–S(5)	109.0 (4)
S(4)–S(5)–S(6)	97.2 (5)	S(5)–S(6)–O(1)	99.6 (11)
S(5)–S(6)–O(2)	102.4 (11)	O(1)–S(6)–O(2)	113.9 (18)
O(3)–S(7)–O(4)	116.5 (20)		

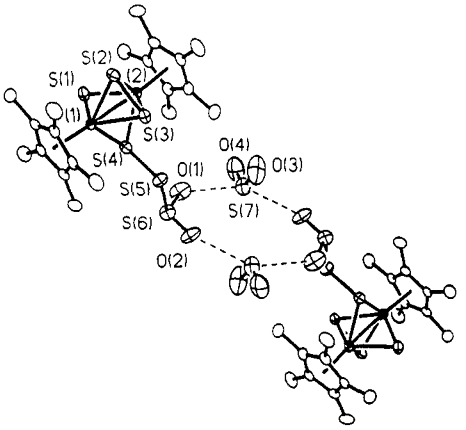


Figure 3. Complete structure of **1**·$2SO_2$, showing cyclic aggregation of SO_2.

significantly less than the shortest intermolecular S–O distance in solid SO_2, 3.10 Å,[9] and also the van der Waals distance, 3.25 Å. The S–O distance in a related weak Lewis acid–base complex, $H_2O\cdots SO_2$, is 2.82 Å (microwave spectroscopy).[10] $Ru(CO)_2(\eta^2\text{-}SO_2\cdot SO_2)(PPh_3)_2$, which contains SO_2 bound to the terminal oxygen of a side-bonded SO_2, has $O\text{–}SO_2$ = 2.51 Å.[1a]

The average value of 1.45 Å for the S–O bonds of the coordinated SO_2 molecule in **1**·$2SO_2$ is somewhat longer than that in free SO_2 (1.43 Å) and that in $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S\cdot SO_2)$ (1.40 Å). However, S–O distances in SO_2 have generally not been a practical measure of bond activation because of inherently large standard deviations.

The $\mu\text{-}SS\text{–}SO_2$ bond is 2.41 Å, considerably shorter than the 2.60 Å in $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S\cdot SO_2)$ which contains SO_2 bound to a bridging sulfide rather than disulfide.[2] This, along with lower SO_2 lability, does clearly indicate a larger degree of electron flow to the SO_2 molecule from the Cr/S system compared to the Mo/S dimer. However, these S–S distances are considerably longer than a "normal" single bond distance (2.04–2.07 Å), and the SSO_2 and $SSSO_2$ units should not be thought of as thiosulfito ligands such as that in $(CN)_5CoSSO_2Co(CN)_5^{6-}$ (S–S = 2.064 Å[11]). Comparing the CrS_5 core distances in **1**·$2SO_2$ with those in **1** shows little change, except for S–S in the $\eta^2\text{-}S_2$ group, which decreases by 0.12 Å on SO_2 binding.

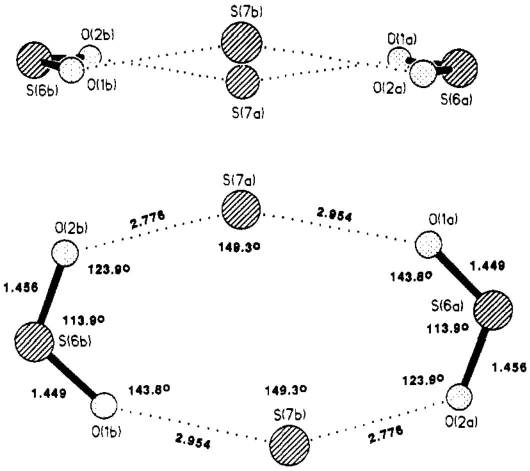
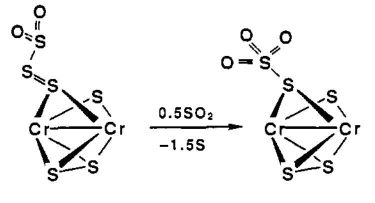


Figure 4. Two views of the ring structure in **1**·$2SO_2$ with distance and angle data. Deviations from plane: S(7a), –0.224; S(6a), –0.015; O(1a), +0.186; O(2a), –0.163 Å (signs reversed for b atoms).

Oxygen-Transfer Reactions of Sulfide–SO_2 Adducts with SO_2 To Form $Cp^*_2Cr_2S_4\cdot SO_3$, 2. The SO_2 adduct of **1** further reacts in solution in the presence of SO_2 to quantitatively give an air-stable green *SO_3* adduct **2**, which can also be viewed as a μ-thiosulfate complex.



1·SO_2 2

(4)

This reaction is notable in that both oxygen transfer *and extrusion of a "core" sulfur* occurs, making this conversion distinct from that in the Mo/S system. Both **2** and also $Cp^*_2Cr_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SS\cdot SO_3)$, the other possible product of eq 4, have previously been prepared by Wachter by reaction of $Cp^*_2Cr_2S_x$ (x = 4, 5) with py·SO_3.[6b] Chemical analysis and X-ray crystallography confirmed that the complex we obtained from eq 4 was indeed **2**. The mechanistic question of whether one oxygen is added to SO_2 to form the SO_3 or whether three oxygens are transferred to the terminal sulfur of the $\eta^2\text{-}S_2$ will be addressed later. SO vibrations were observed in the Nujol mull IR spectrum of **2** at 1228, 1204, 1012, and 610 cm^{-1}, similar to those reported by Wachter.[6b] Mass spectroscopy of **2** (chemical ionization or electron impact) did not show a parent ion peak, but a cluster of peaks centered at mass 502 corresponding to the fragment $Cp^*_2Cr_2S_4$ was seen. An electron impact spectrum of the product mixture of eq 4 was used to confirm that S_8 was formed (a mass 256 peak was present that was not seen in the spectrum of isolated **2**).

The reaction in eq 4 occurs at a much faster rate than the thiosulfate formation in the Mo/S system (eq 2). Under identical

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(9) Post, B.; Schwartz, R. S.; Fankuchen, I. *Acta Crystallogr.* **1952**, *5*, 372.

(10) Matsumura, K.; Lovas, F. J.; Suenram, R. D. *J. Chem. Phys.* **1989**, *91*, 5887.

(11) Fronczek, F. R.; Marsh, R. E.; Schaefer, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 3382.

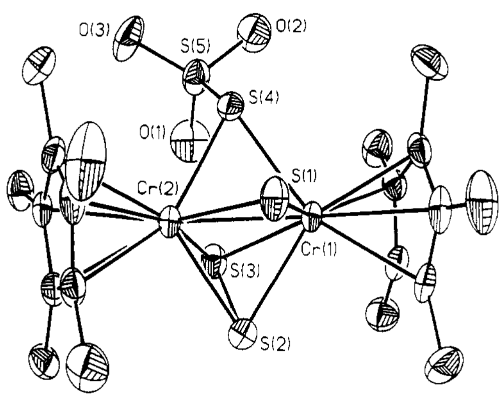


Figure 5. ORTEP drawing (50% ellipsoids) of the structure of $Cp^*_2Cr_2S_5\cdot SO_3\cdot CD_3OD_{lattice}$.

Table IV. Bond Lengths (Å) and Angles (deg) for **2**

Bond Lengths			
Cr(2)–Cr(1)	2.505 (1)	Cr(2)–S(3)	2.336 (1)
Cr(2)–S(1)	2.227 (1)	Cr(2)–S(4)	2.361 (2)
Cr(2)–S(2)	2.320 (1)	Cr(2)–C(11)	2.219 (5)
Cr(2)–C(12)	2.219 (6)	Cr(2)–C(13)	2.237 (5)
Cr(2)–C(14)	2.246 (4)	Cr(2)–C(15)	2.230 (4)
Cr(1)–S(3)	2.334 (1)	Cr(1)–S(1)	2.230 (1)
Cr(1)–S(4)	2.374 (1)	Cr(1)–S(2)	2.309 (2)
Cr(1)–C(1)	2.236 (5)	Cr(1)–C(2)	2.234 (3)
Cr(1)–C(3)	2.218 (4)	Cr(1)–C(4)	2.218 (6)
Cr(1)–C(5)	2.226 (6)	S(3)–S(2)	2.033 (2)
S(4)–S(5)	2.152 (2)	S(5)–O(1)	1.436 (4)
S(5)–O(2)	1.445 (6)	S(5)–O(3)	1.443 (3)
Bond Angles			
Cr(1)–Cr(2)–S(3)	57.5 (1)	Cr(1)–Cr(2)–S(1)	55.9 (1)
S(3)–Cr(2)–S(1)	112.5 (1)	Cr(1)–Cr(2)–S(4)	58.3 (1)
S(3)–Cr(2)–S(4)	80.7 (1)	S(1)–Cr(2)–S(4)	74.4 (1)
Cr(1)–Cr(2)–S(2)	57.0 (1)	S(3)–Cr(2)–S(2)	51.8 (1)
S(1)–Cr(2)–S(2)	83.2 (1)	S(4)–Cr(2)–S(2)	113.2 (1)
C(14)–Cr(2)–C(15)	37.1 (1)	Cr(2)–Cr(1)–S(3)	57.6 (1)
Cr(2)–Cr(1)–S(1)	55.7 (1)	S(3)–Cr(1)–S(1)	112.4 (1)
Cr(2)–Cr(1)–S(4)	57.8 (1)	S(3)–Cr(1)–S(4)	80.5 (1)
S(1)–Cr(1)–S(4)	74.1 (1)	Cr(2)–Cr(1)–S(2)	57.4 (1)
S(3)–Cr(1)–S(2)	51.9 (1)	S(1)–Cr(1)–S(2)	83.4 (7)
S(4)–Cr(1)–S(2)	113.1 (1)	Cr(2)–Cr(1)–C(1)	144.4 (1)
Cr(2)–S(3)–Cr(1)	64.9 (1)	Cr(2)–S(3)–S(2)	63.7 (1)
Cr(1)–S(3)–S(2)	63.4 (1)	Cr(2)–S(1)–Cr(1)	68.4 (1)
Cr(2)–S(4)–Cr(1)	63.9 (1)	Cr(2)–S(4)–S(5)	115.4 (1)
Cr(1)–S(4)–S(5)	116.5 (1)	Cr(2)–S(2)–Cr(1)	65.5 (1)
Cr(2)–S(2)–S(3)	64.5 (1)	Cr(1)–S(2)–S(3)	64.7 (1)
S(4)–S(5)–O(1)	108.0 (2)	S(4)–S(5)–O(2)	102.6 (2)
O(1)–S(5)–O(2)	113.3 (3)	S(4)–S(5)–O(3)	103.1 (2)
O(1)–S(5)–O(3)	114.5 (3)	O(2)–S(5)–O(3)	113.9 (3)

conditions (toluene, 1% Et_3N, 25 °C), the above conversion takes place in 10 min, but negligible conversion of $Cp^*_2Mo_2S_4\cdot SO_2$ to $Cp^*_2Mo_2S_4\cdot SO_3$ takes place even after months. Higher solvent polarity combined with the presence of Lewis base promoters such as Et_3N increases reaction rates in both systems by orders of magnitude. Even for the Cr/S system conversion to the thiosulfate did not occur after several hours in either toluene or chlorobenzene until a small amount of amine ($\sim$1%) or methanol cosolvent ($\sim$1:1) was added. The brown-red PhCl solution of $\mathbf{1}\cdot 2SO_2$ converted to green **2** in 10 min in the presence of MeOH at room temperature and nearly instantaneously if Et_3N was added.

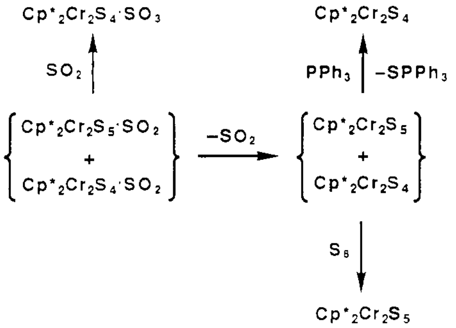
$Cp^*_2Cr_2S_4$ was also shown to transform to **2** rapidly in SO_2-saturated organic solvents, indicating that the extra sulfur in **1** was not a major factor in comparisons to the Mo system. The reaction rates were much higher for the CrS_4 complex than those of the directly analogous MoS_4 complex. In $CDCl_3$, an NMR tube reaction showed 50% conversion to **2** within 1 h, whereas for the Mo congener <5% reaction occurred even after 1 week. Addition of a weak base and/or more polar solvent such as MeOH to the $CDCl_3$ solutions speeded up the conversions markedly: completion within 15 min for the Cr system and 3 h for Mo. The higher reaction rates for the chromium sulfides clearly demonstrate that the nature of the metal is still important in this chemistry, even though the conversions appear to occur only on the sulfide ligands without direct involvement of the metal. The reaction rates are higher for the complexes with lower ν_{SO} IR frequency and longer observed S—O bond length, i.e., more activated S=O: $Cp^*_2Cr_2S_5\cdot SO_2$ (ν_{SO} = 1210, 1060 cm^{-1}; S—O = 1.45 Å) > $Cp^*_2Mo_2S_4\cdot SO_2$ (ν_{SO} = 1230, 1080 cm^{-1}; S—O = 1.40 Å) > $Cp^*_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2C_2H_2)\cdot SO_2$ (ν_{SO} = 1240, 1090 cm^{-1}; no reaction, possibly because of less flexible sulfide core[2]).

Crystal Structure of $\mathbf{2\cdot CD_3OD}$. Crystals of **2** as dark green pyramids containing a lattice solvent molecule were grown from a concentrated MeOH-d_4 NMR sample solution by allowing it to stand at room temperature for several days, and the structure was determined at 25 °C. The molecular geometry (Figure 5) is nearly identical to that of the Mo analogue $Cp^*_2Mo_2S_4\cdot SO_3$.[2] Bond distances and angles are given in Table IV. The structures of $Cp^*_2M_2S_4\cdot SO_3$ showed that the S=O and S—SO_3 bond lengths are quite similar, i.e., 1.43 and 2.15 Å for M = Cr and 1.44 and 2.17 Å for M = Mo.

The orientation of the various groups (S, SO_2, SO_3) attached to the μ-S in these M_2S_4 core units is worthy of comment. In all cases only one isomer is present, the exo form (group pointed toward the η^2-S_2), except for *endo*-$Cp^*_2Mo_2S_4\cdot SO_2$. This stereoselectivity may be significant in mechanistic pathways (see below).

Improved Synthetic Routes to Chromium Sulfide Complexes. Preparation of 1 by Reaction of $\mathbf{Cp^*_2Cr_2S_4}$ with $\mathbf{S_8}$. Reaction of $Cp^*_2Cr_2S_4$ with S_8 in chloroform or toluene solution was found to quantitatively (by NMR) produce **1** within 5 min. This reaction has not previously been reported and proved to be a convenient method of incorporating ^{34}S into the Cr/S core for mechansitic studies (see below). Also, a new, attractive method of producing **2** and, potentially, $Cp^*_2Cr_2S_x$ (x = 4, 5) in pure form without having to use column chromatography was found. The published procedure[5] for the preparation of **1** is followed, but the crude reaction product mixture is reacted with SO_2 to precipitate $\mathbf{1}\cdot 2SO_2$ (containing a small amount of **2** and perhaps $Cp^*_2Cr_2S_4\cdot SO_2$). Unreacted starting material $[Cp^*Cr(CO)_2]_2$ present in the reaction mixture does not react with SO_2 as shown in a separate experiment. The SO_2 adduct can then readily be converted to pure **2** by further reaction with SO_2.

This procedure can also be applied to synthesizing pure $Cp^*_2Cr_2S_4$ or **1**. In order to avoid formation of **2**, the SO_2 adduct(s) formed must be precipitated *immediately*. They are then dissolved in toluene, and full vacuum is quickly applied while stirring in order to remove all SO_2. A mixture of the S_5 and S_4 (minor) complexes is formed, and reaction with Ph_3P, which removes sulfur from **1**,[6] can then be used to produce exclusively $Cp^*_2Cr_2S_4$. Reaction of the mixture with S_8 would produce pure **1** on the other hand. The following scheme summarizes the transformations:



Proposed Mechanism of the Oxygen-Transfer Reaction. How does oxygen atom transfer take place in solution to produce the

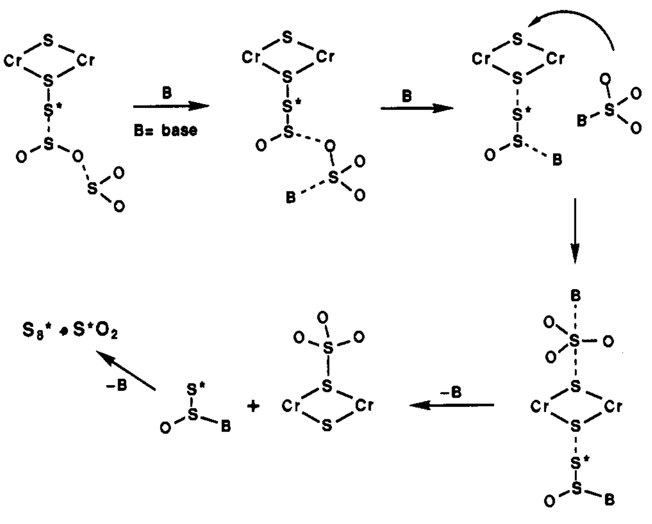


Figure 6. Possible mechanism for the disproportionation of SO_2 to sulfur and SO_3 based on the structure of **1**·2SO_2, where B is a Lewis base such as MeOH or Et_3N. S* indicates the position of ^{34}S in the labeling experiment (metal-bound sulfurs also contained ^{34}S; η^2-S_2 group not shown for clarity).

SO_3 group from SO_2? A possible scenario could involve oxygen atom transfer from sulfide-coordinated SO_2 to weakly-associated SO_2 molecules analogous to those in the crystal structure of **1**·2SO_2. Figure 6 illustrates a mechanism for half the "tetrameric" unit of Figure 3 that would more realistically be present in solution (the position and ultimate fate of the terminal sulfur of the η^1-S_2 is marked with an asterisk, which also refers to ^{34}S labeling below). Lewis bases [B], such as amines, must also play a role because they have been shown to accelerate both the SO_2 disproportionation and catalytic hydrogenation (eqs 1 and 2) and proven to function in Lewis rather than Bronsted fashion.[2] For example, they could trigger the oxygen transfer (which does not occur in the solid state) by stabilizing nascent Lewis acid fragments such as SO_3 and S_2O. This could lower the activation barrier and make the thermodynamics more favorable (SO_2 disproportionation to SO_3 and S_8 is endothermic by 38 kcal/mol,[12] but energy could be regained by B–SO_3 interactions and ultimately formation of S–SO_3). A BSO_3 group could displace the presumably weakly-held S_2O fragment remaining attached to the μ-S (it is best to view this fragment as μ-S···S*SO rather than μ-SS*···SO in light of the ultimate elimination of S* as S_8 as proven below). The process could be stepwise or concerted and possibly involve immediate attack at the more sterically-accessible *adjacent* μ-S, leading to formation of the exo isomer observed for both chromium and molybdenum thiosulfates. A *concerted* displacement would rationalize why the known[6b] complex $Cp^*{}_2Cr_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SS{\cdot}SO_3)$ is not observed as a product. The latter would likely result if any SO_3 or B–SO_3 was set free and then attacked unreacted **1**·2SO_2.

Regarding the displaced S_2O, lower oxides of sulfur are known to be unstable and to rapidly disproportionate to SO_2 plus elemental sulfur,[13] the other final product of the oxygen transfer. S_2O has been reported[14] to form a 1:1 adduct with Me_3N at −30 °C, decomposing within seconds at 20 °C to S_8, SO_2, and amine. It is possible that a base helps to extract the S_2O group from the μ-S, though this may not be necessary.

Sulfate was not formed from **1**·2SO_2, although the cyclic SO_2 aggregate appears set up for it. Sulfate has been found to be produced by oxygen transfer involving metal-bound SO_2, notably in $Ru(CO)_2(\eta^2\text{-}SO_2{\cdot}SO_2)(PPh_3)_2$, which as in **1**·2$SO_2$ contains SO_2 weakly interacting with the terminal oxygen of a bound SO_2. In O_2-free solutions containing SO_2, $Ru(CO)_2(SO_4)(PPh_3)_2$ and Ph_3PS spontaneously formed.[1a] It is interesting that PPh_3, derived either sacrificially or from added PPh_3, acts as a sulfur scavenger and perhaps aids oxygen transfer.

^{34}S Isotopic Labeling Studies of the Oxygen-Transfer Reaction and Sulfide Ligand Scrambling. In order to support the mechanism proposed in Figure 6, ^{34}S-labeling studies were carried out to determine if reaction of $Cp^*{}_2Cr_2(\mu\text{-}S)(\mu\text{-}\eta^2\text{-}S_2)(\mu\text{-}\eta^1\text{-}S^{34}S)$ with SO_2 produces nonlabeled **2** and ^{34}S-labeled S_8. The labeled complex was prepared by the facile reaction of $Cp^*{}_2Cr_2S_4$ with $^{34}S_8$ in $CHCl_3$ or toluene. A 4-fold excess of sulfur was used; slow solvent removal (~3 h total reaction time) gave a solid residue containing **1** and unreacted sulfur (total coordinated and free $^{34}S/^{32}S = 1$). Mass spectroscopy was used to monitor the position of the label. Surprisingly, the chemical ionization mass spectrum of the solid showed that *^{34}S was incorporated into all five of the sulfur sites; i.e., the core sulfurs about the metal completely exchange with each other.* Two sets of fragmentation patterns were seen: one attributable to fragments of the complex with higher mass than expected for $Cp^*{}_2Cr_2S_4{}^{34}S$ and those attributable to scrambled sulfur (isotopomers of S_8). Although the parent ion peak of the complex is very weak, the envelope centered at mass 507 corresponded to all isotopomers of the $Cp^*{}_2Cr_2S_4$ fragment (parent minus S) consistent on the average with roughly equal amounts of ^{34}S and ^{32}S. The analogous spectrum of unlabeled **1** showed the envelope centered at mass 503 by comparison. Thus, it would be appropriate to write the product of the above reaction as a mixture of molecules with the formula $Cp^*{}_2Cr_2{}^xS_5$ (x = 160, 162, 164, 166, 168, and 170). As far as we know there have been no previous demonstrations of complete sulfur interchange in polysulfido complexes. As a further check, isolated **1** and $^{34}S_8$ were found to totally exchange sulfurs in $CHCl_3$ overnight, but as expected, **2** did not incorporate $^{34}S_8$.

The mixture of scrambled S_8 and $Cp^*{}_2Cr_2{}^xS_5$ as obtained above was reacted with SO_2, and the resulting adduct (^{34}S-labeled **1**·2SO_2) was isolated and washed well with CS_2 to remove the S_8 and any uncomplexed $Cp^*{}_2Cr_2{}^xS_5$ (both **1**·2SO_2 and **2** are insoluble in CS_2). Mass spectroscopy of this solid confirmed the absence of elemental sulfur that would interfere with isotopic analysis of sulfur from subsequent reactions. Reaction of the labeled adduct with SO_2 in $CHCl_3$–MeOH followed by solvent removal gave a solid residue containing the $Cp^*{}_2Cr_2{}^xS_4{\cdot}SO_3$ adduct *unlabeled in the SO_3 position* (see IR results below) plus *^{34}S-labeled* S_8, thus supporting the proposed mechanism. The mass spectrum of the residue showed two sets of fragmentation patterns: one attributable to $Cp^*{}_2Cr_2{}^xS_4$ (the parent ion $Cp^*{}_2Cr_2{}^xS_4{\cdot}{}^{32}SO_3$ was again not seen) and one for isotopically-scrambled S_8. These data thus refute formation of the SO_3 group by transfer of three oxygens to the terminal sulfur of the S_2 ligand, which would produce $^{34}SO_3$ and *unlabeled* S_8 originating solely from oxygen-stripped SO_2.[15]

$$\mathrm{Cr_2\text{-}\mu\text{-}S\text{-}^{34}S + 1.5SO_2 \not\longrightarrow Cr_2\text{-}\mu\text{-}S\text{-}^{34}SO_3 + 1.5S} \tag{5}$$

The identification of the SO_3 adduct as $Cp^*{}_2Cr_2{}^xS_4{\cdot}{}^{32}SO_3$ and not $Cp^*{}_2Cr_2{}^xS_4{\cdot}{}^{34}SO_3$ utilized infrared spectroscopy, which gave ν_{SO} bands identical to those of an authentic sample of unlabeled SO_3 adduct. Judging by calculations[16] and the fact that $^{32}SO_2$ gives ν_{SO} bands at 1151 and 1361 cm^{-1} versus 1146 and 1344 cm^{-1} for $^{34}SO_2$,[8] resolvable shifts in the SO_3 vibrational modes would have been expected in $Cp^*{}_2Cr_2{}^xS_4{\cdot}{}^{34}SO_3$.

Reactivity of 2 with Bases and H_2 Compared to that of the Mo Analogue. The SO_3 group in **2** is not as easily removed by weak

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[12] Calculated from the standard ΔG's of formation for $3SO_2\ (g) \rightarrow 2SO_3\ (g) + S\ (g)$.

[13] Tang, S.-Y.; Brown, C. W. *Inorg. Chem.* **1975**, *14*, 2856 and references therein.

[14] Schenk, P. W.; Steudel, R. *Z. Anorg. Allg. Chem.* **1966**, *342*, 263.

[15] It is unlikely that any significant scrambling between product sulfur and $Cp^*{}_2Cr_2{}^xS_5{\cdot}SO_2$ reactant would occur in the short time frame of the reaction (<10 min).

[16] For $Cp^*{}_2Cr_2S_4{\cdot}{}^{34}SO_3$, the expected SO frequencies based on calculation would be approximately 1216, 1192, 1002, and 604 cm^{-1} (shifted down from 1228, 1204, 1012, and 610 cm^{-1}).

Lewis bases [B] as that in the Mo analogue (eq 6). Thus, while

$$Cp^*_2M_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3) \xrightarrow{[B],\ 25\text{-}75\ ^\circ C} Cp^*_2M_2(\mu\text{-}S_2)(\mu\text{-}S)_2 + [B]SO_3 \quad (6)$$

complete conversion was observed for $Cp^*_2Mo_2S_4{\cdot}SO_3$ in 1:4 $CDCl_3$–Et_3N at 25 °C in 18 h,[2] little reaction took place for the Cr analogue under similar conditions, even after 5 days. Whereas 85% SO_3 removal was observed for $Cp^*_2Mo_2S_4{\cdot}SO_3$ in MeOH at 75 °C for 1.5 h, no conversion took place for the Cr analogue. This great reactivity difference between Cr and Mo congeners was expected to be reflected in a significant disparity in the S–SO_3 or even S–O bond lengths. Surprisingly, the structure of **2** showed that these bond lengths are almost identical for Cr and Mo. Why then is there such a large reactivity difference? Since the only variance between these two species is the nature of the metal, and this does not induce any structural differences on the S–SO_3 and S–O bonds, indirect influences might be a factor. A reviewer suggested that internal electron-transfer reactions (formation of S–S bonds between μ-S ligands and concomitant metal reduction) are very facile for molybdenum polysulfides and could assist SO_3 dissociation. However, it is important to note that the ^{34}S interchange between sulfide and disulfide ligands in $Cp^*_2Cr_2S_5$ implies that *internal redox processes also occur for chromium sulfides*. Steric factors might be a consideration, since the Cr complex has a more crowded coordination sphere (M–M and M–S distances are ca. 0.1 Å shorter for the Cr complex than the Mo analogue).

Reaction of **2** with hydrogen was very sluggish, also unlike that for the Mo analogue (eq 3). In an NMR tube experiment, a solution of **2** in PhCl containing a small amount of Et_3N promoter showed no reaction after several days under an H_2 atmosphere. Only under vigorous conditions (160 °C, 2 h) was it converted to **1**, which probably results from reaction of $Cp^*_2Cr_2S_4$, the expected product, with sulfur (a primary or secondary product of hydrogenation of **2**).

In regard to H_2 activation by sulfide complexes, the dinuclear Mo systems are unique in their ability to split H_2 to give SH ligands such as those in $[Cp^*Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$.[17] It is probable that in eq 3 SH groups actually reduce the SO_3 in $Cp^*_2Mo_2S_4{\cdot}SO_3$ because $Cp^*_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$ was found[2] to quantitatively reduce the latter to $Cp^*_2Mo_2S_4$ (a rare example of reaction between two metal complexes to form *one* complex):

$$Cp^*_2Mo_2S_4{\cdot}SO_3 + Cp^*_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2 \rightarrow 2Cp^*_2Mo_2S_4 + H_2O + SO_2 \quad (7)$$

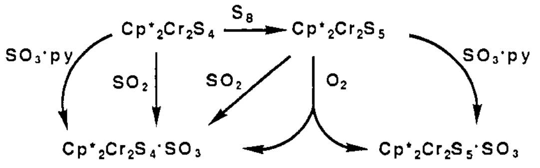
$Cp^*_2Mo_2S_4$ rapidly reacts with H_2 to regenerate the SH complex, so only a trace amount of it or another species capable of producing SH ligand, perhaps the thiosulfate itself, may be all that is needed to catalyze SO_3 reduction. The very slow reaction of $Cp^*_2Cr_2S_4{\cdot}SO_3$ with H_2 as well as the ineffectiveness of the chromium sulfides in catalyzing SO_2–H_2 reaction (see below) can possibly be correlated with their inability to split H_2 to Cr–SH species.

Catalytic Activity of 1 toward SO_2–H_2 Reaction Compared to the Mo System. As shown in eq 1 and Figure 1, $Cp^*_2Mo_2S_4$ catalyzed hydrogenation of SO_2 in 1:1 chlorobenzene–butanol at 75 °C at a rate of 350 turnovers/h.[2,4] Using exactly the same conditions (closed 250-mL glass reactor containing ~7 mmol of SO_2, ~3 atm of H_2, and Bu_3N promoter), **1** was tried as a catalyst. As observed by characteristic color changes, the catalyst solution (23 mg of **1**/25 mL) immediately transformed to the red-brown SO_2 adduct on exposure to the SO_2–H_2 mixture. About 15 min later at 75 °C, it became bright green, indicative of the thiosulfate **2**. The hydrogenation reaction was monitored by a pressure gauge, but no noticeable pressure drop occurred after 1 h (complete reduction of SO_2 occurred within this time for the Mo system). After 16 h only partial reduction took place, equivalent to a rate of 1–2 turnover/h, consistent with the above-discussed slow H_2 reduction of **2**, a key step in the proposed catalytic cycle (Figure 1). Raising the temperature of the reaction system to 160 °C led to catalyst deactivation.

Summary and Conclusions

The shift from molybdenum to chromium sulfide complexes has proven to be very fruitful, providing new evidence for how oxygen transfer takes place in the $\mu\text{-}S{\cdot}SO_2 + 0.5SO_2 \rightarrow \mu\text{-}SSO_3 + 0.5S$ reaction. In addition, it was established by ^{34}S labeling that complete sulfide ligand interchange occurs in $Cp^*_2Cr_2S_5$, **1**, probably via internal redox reactions similar to those well-known for molybdenum polysulfides. The labile, terminally-bound sulfur of the η^1-S_2 ligand in **1** is the active site in the SO_2 disproportionation process (eq 4) and is eventually eliminated, making this system distinct from $Cp^*_2Mo_2S_4$. As a result, further insight into mechanistic questions was gained, amplified by the finding of SO_2 aggregation in $Cp^*_2Cr_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SS{\cdot}SO_2){\cdot}SO_2$, **1**·$2SO_2$. It appears that association of SO_2 molecules by weak Lewis acid–base binding is the first step in the SO_2 disproportionation. The sulfur in SO_2 is a relatively strong electron acceptor while its oxygens are weak electron donors. One SO_2 molecule attaches itself to a sulfide ligand of **1** by accepting electrons, which then makes its oxygens more electron-rich (nucleophilic) and invites a second and perhaps a third SO_2 molecule (as in **1**·$2SO_2$) to bind to them via the electrophilic sulfur atom (Figure 6). Cleavage of an S–O bond on the first SO_2 molecule and transfer of an oxygen to the second then gives SO_3 plus S_2O (if one includes here the original terminal S of the S_5 core), a process that could be promoted by interaction of the nascent SO_3 and/or S_2O with Lewis bases [B], e.g., R_3N. In the absence of added base, adventitious water or even another SO_2 molecule (oxygen lone pair) could less effectively fulfill the role. The mechanism in Figure 6 would then be consistent with several crucial observations, foremost being ultimate extrusion of the terminal sulfur of the CrS_5 core as S_8, confirmed by ^{34}S labeling. The expulsion of the maximum amount of sulfur from the CrS core, i.e., the lack of formation of $Cp^*_2Cr_2(\mu\text{-}S)(\mu\text{-}S_2)(\mu\text{-}SS{\cdot}SO_3)$, indicates that, as found in several other systems, the μ-thiosulfate ligand is a thermodynamically favored species.[2] This mechanism could also be applicable to SO_2 disproportionation on the $Cp^*_2M_2S_4$ (M = Cr, Mo) systems, whereby the only difference would be formation of equally unstable SO instead of S_2O.

It is interesting to note that *air oxidation* of **1** (toluene, 45 °C, 18 h) has also been found to yield thiosulfates, in this case a *mixture* of **2** and $Cp^*_2Cr_2S_5{\cdot}SO_3$.[6b] The following scheme summarizes thiosulfate formation from this and other reactions by Wachter's and our groups:



Reaction of $Cp^*_2Mo_2S_4$ and O_2 had earlier given $Cp^*_2Mo_2S_4{\cdot}SO_3$ (~20% yield),[2,18] and the SO_2 oxygen-transfer process was considered as a candidate for the mechanism of thiosulfate formation (SO_2 generated by sacrificial air oxidation of sulfide). However, both the observation of negligible SO_2 in a $Cp^*_2Mo_2S_4$–

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(17) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1.

(18) (a) Brunner, H.; Klement, U.; Pfauntsch, J.; Wachter, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 230. (b) Brunner, H.; Kauermann, H.; Pfauntsch, J.; Wachter, J. *J. Organomet. Chem.* **1987**, *331*, 45.

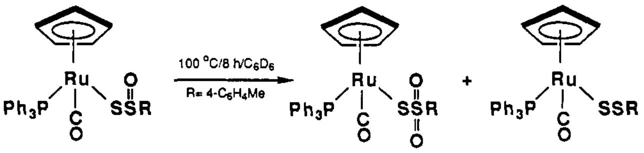
air reaction mixture[2] and the difference in products from reaction of **1** with O_2 versus SO_2 suggest that another mechanism[19] operates.

It is conceivable that other types of reactions of SO_2, with or without metal complexes present, may actually occur via a disproportionation route. Indeed FeS has been found to react with SO_2 in aqueous media to produce *thiosulfate* ion and Fe^{2+}.[20] The initial step in the reaction was believed to be adsorption of SO_2 on FeS, followed by dissolution of the FeS with the formation of Fe^{2+} ion and thiosulfurous acid intermediate, $H_2S_2O_2$. The latter then was proposed to react with HSO_3^- to give thiosulfuric acid, $H_2S_2O_3$, and HSO_2^-. All of these species are very unstable though, and an oxygen-transfer route could be an alternate *direct* pathway to $FeSSO_3$ without involvement of protons. The role of Lewis bases in promoting these reactions could be fulfilled by H_2O here. In this regard, the industrially important Claus-type reaction (eq 8), for which the mechanism is not well understood, does not require a metal catalyst but does require the presence of water or other basic media (alcohols, alumina).[21] Equation 8 does not occur or is slow in hydrocarbons or halogenated solvents,[21a,b] and we have noted a similar profile for the group 6 sulfide–SO_2 reactions. One could envision formation of an $H_2S{\cdot}SO_2$ adduct which undergoes oxygen transfer to give S_8 and $H_2S{\cdot}SO_3$. The latter is essentially thiosulfuric acid, which is known[22] to decompose in the presence of water to species such as sulfur, H_2O, and SO_2 which are products/reactants of the Claus reaction.

$$2H_2S + SO_2 \rightarrow {}^3/_8S_8 + 2H_2O \qquad (8)$$

Although the rate of SO_2 disproportionation on the Cr sulfides is much faster than that of the Mo analogue, the resulting complex **2**, $Cp^*{}_2Cr_2S(S_2)(SSO_3)$, is less reactive toward Lewis bases and H_2 than the Mo congener. Apparently the low reactivity with H_2 and the ineffectiveness of the chromium sulfides in catalyzing SO_2 hydrogenation can be correlated with the inability of chromium sulfides to readily form Cr–SH species.

The SO_2 disproportionation appears to be entirely a Lewis acid–base process, with the metal perhaps serving only as electron ballast. Recently a possibly related oxygen atom disproportionation process was reported[23] for thiosulfinato to thiosulfonato conversion:



(9)

It is thus becoming increasingly evident that SO_2 and possibly other oxygen-containing small molecules (e.g., NO_x)[24] with amphoteric acid–base properties may be more susceptible to cleavage reactions than previously thought. Further studies of the mechanisms of such reactions may lead to new strategies for chemical synthesis and, more importantly, abatement of environmentally damaging oxides.

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Supplementary Material Available: Tables of structure determination data, fractional coordinates, and general displacement parameter expressions (*U*'s) (9 pages). Ordering information is given on any current masthead page.

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(19) As originally proposed by Wachter (ref 18), SO_3 (or an SO_3 source analogous to $py{\cdot}SO_3$) is probably formed in some unidentified fashion and randomly binds to either S_4 or S_5 species (the former possibly generated from the latter by sacrificial loss of its labile sulfur to air oxidation).

(20) Thom, G. C.; Waters, P. F.; Hadermann, A. F. *Inorg. Chem.* **1978**, *17*, 1693.

(21) (a) Matthews, E. *J. Chem. Soc.* **1926**, 2270. (b) Albertson, N. F.; McReynolds, J. P. *J. Am. Chem. Soc.* **1943**, *65*, 1690. (c) Gregor, I. K.; Martin, R. L. *Aust. J. Chem.* **1959**, *12*, 424. (d) Datta, A.; Cavell, R. G. *J. Phys. Chem.* **1985**, *89*, 454.

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(23) Shaver, A.; Plouffe, P.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 7780.

(24) Oxygen transfer from NO_2 to a μ-S ligand to form μ-SO_2 has recently been reported: Qi, J.-S.; Schrier, P. W.; Fanwick, P. E.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1737.