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Peracid Oxidation of Inorganic Chalcogen Ligands in Transition Metal Complexes

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The use of organic peracids as rapid, selective oxidation agents for coordinated chalcogens, η^2-E_2 (E = S, Se) and μ_3-E (E = S, Se, Te), has been examined. Stepwise oxidation of $[Ir(\eta^2\text{-}S_2)(dppe)_2]PF_6$ with *m*-chloroperbenzoic acid (*m*-CPBA) yielded $[Ir(\eta^2\text{-}S_2O)(dppe)_2]PF_6$ (**1**) and $[Ir(\eta^2\text{-}S_2O_2)(dppe)_2]PF_6$ (**2**). Facile oxidation of $[Ir(\eta^2\text{-}Se_2)(dppe)_2]PF_6$ and $Cp_2Nb(\eta^2\text{-}S_2)Cl$ with peracetic acid produced $[Ir(\eta^2\text{-}Se_2O)(dppe)_2]PF_6$ (**3**) and $Cp_2Nb(\eta^2\text{-}S_2O)Cl$ (**4**). Similarly, reaction of $Fe_3(\mu_3\text{-}S)_2(CO)_9$ and $Fe_2Pt(\mu_3\text{-}E)_2(CO)_6(PPh_3)_2$ (E = S, Se, Te) with *m*-CPBA produced the chalcogen monoxide complexes, $Fe_3(\mu_3\text{-}SO)(\mu_3\text{-}S)(CO)_9$ (**5**) and $Fe_2Pt(\mu_3\text{-}EO)(\mu_3\text{-}E)(CO)_6(PPh_3)_2$ (**6**). The stereochemistry and reactivity of all of these complexes have been studied. Reaction of the η^2-S_2O complexes with nucleophiles (Nu = PPh_3, CH_3NC) revealed sulfur transfer as the favored reaction and the unsubstituted sulfur donor atom as the most reactive site. Attempted formation of η^1- or η^2-SO complexes by selective sulfur-abstraction reactions was unsuccessful, but an unsymmetrical dichalcogenide complex, $[Ir(\eta^2\text{-}SSe)(dppe)_2]^+$ (**7**), was synthesized from $[Ir(dppe)_2]Cl$ and $Cp_2TiS_xSe_{5-x}$ ($x \approx 3$). Examination of the oxygen-transfer capabilities of the iridium complexes revealed the following trend: $Se_2O >> S_2O_2 > S_2O$. In solution, the $[Ir(Se_2O)(dppe)_2]PF_6$ complex spontaneously eliminates the exocyclic oxygen to yield $[Ir(Se_2)(dppe)_2]^+$ and oxidizes C_2H_5SH to ethyl disulfide. In contrast, the $[Ir(S_2O)(dppe)_2]Cl$ and $Cp_2Nb(S_2O)Cl$ complexes show a pronounced tendency toward sulfur transfer to substrates but virtually no oxygen-transfer capability. The μ_3-SO complexes proved to be virtually inert toward both O- and S-transfer reactions. Also described is the utility of chiral solvating and lanthanide shift reagents in the elucidation of the structure and stereochemistry of $Cp_2Nb(S_2O)Cl$ using ^1H NMR spectroscopy.

Introduction

In recent years, increasing attention has been directed toward the generation and synthetic utility of non-metal oxo ligands. Representative of the more fruitful aspects of this trend are studies on the potential use of the $MNO-MNO_2$ interconversion as oxidation catalysts,[1] the activation of iodosobenzene by metalloporphyrins,[2] and the significant body of work on the coordination chemistry of sulfur dioxide.[3] It was in this spirit that we set out to examine the relatively unexplored basic coordination chemistry of the lower sulfur and selenium oxides.

In the now classic work, Schmid et al. found that $[Ir(S_2)(dppe)_2]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) undergoes periodate oxidation giving $[Ir(S_2O_2)(dppe)_2]^+$, which was characterized by X-ray diffraction.[4] This S_2O_2 complex reacts with triphenylphosphine to give triphenylphosphine oxide and $[Ir(S_2O)(dppe)_2]^+$ with the disulfur-bound S_2O unit exhibiting η^2-coordination.[5] Although the S_2O ligand is closely related to the more prevalent SO_2 ligand, the analogous $[Ir(SO_2)(dppe)_2]Cl$ complex exhibits properties consistent with a monodentate, pyramidal sulfur dioxide ligand.[6] The only authenticated sulfur monoxide complex is $Fe_3(S)(SO)(CO)_9$,[7] although several other complexes are claimed to contain this ligand.[8,9]

Certain aspects of selenium oxide chemistry have received considerable scrutiny as a consequence of the great utility of selenium dioxide,[10] selenoxides (R_2SeO), and seleninic acids ($RSeO_2H$) in organic synthetics.[11] An additional area of interest derives from biochemical studies where, for example, a selenenic acid unit (RSeOH) is postulated as the active site in glutathione peroxidase.[12] Practically nothing is known of the coordination chemistry of selenium oxide systems including SeO_2. Examples of diselenium oxide units (–SeSe(O)–) are particularly rare, with the preparation and preliminary characterization of the first organoselenolseleninates (RSeSe(O)R) being very recent.[13]

The published syntheses of the S_2O_2 and S_2O complexes are inefficient and in the case of $Fe_3(SO)S(CO)_9$, actually artifactual. In this paper, we describe a general and high-yield route to Schmid's iridium compounds and the extension of this methodology for the synthesis of new examples of E_xO_y (E = S, Se) complexes. Furthermore, we describe the results of the isolation of a stable η^2-SSe compound and unsuccessful quest for examples of a η^2-SO complex.

Results and Discussion

Oxidation of η^2-E_2 Ligands (E = S, Se). We have found that organic peracids will rapidly and selectively oxidize *inorganic* sulfur, selenium, and tellurium ligands. This finding parallels the utility of peracids for the oxidation of elemental sulfur,[14] and organic sulfides[15] and a previous report by Balch et al., concerning the oxidation of a bridging sulfide ligand.[16]

The monooxidation of $[Ir(S_2)(dppe)_2]PF_6$ with *m*-chloroperbenzoic acid (*m*-CPBA) occurs within seconds at ~0 °C

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Table I. ^{1}H NMR Chemical Shift (δ) Data[a]

complex	high-field ortho phenyl protons[b]	Cp_a, Cp_a*	Cp_b, Cp_b*	solvent
$[Ir(S_2O)(dppe)_2]^+$	6.40 (1.8 H), 6.46 (1.8 H)			CD_3NO_2
$[Ir(S_2O_2)(dppe)_2]^+$	6.20 (3.6 H)			CD_2Cl_2
$[Ir(Se_2O)(dppe)_2]^+$	6.28 (1.8 H), 6.76 (1.9 H)			$CDCl_3/CD_3NO_2$ (3:1 v/v)
$[Ir(SSe)(dppe)_2]^+$	6.20, 5.93[c]			$CDCl_3$
$Cp_2Nb(S_2O)Cl$ (4)		5.98 (5 H)	5.87 (5 H)	$CDCl_3$
4 (ASIS effect)		5.36 (5 H)	4.99 (5 H)	$C_6D_6/CDCl_3$ (3:1 v/v)
4 + 6.0 equiv of ROH*[e]		5.84 (2.5 H), 5.83 (2.5 H)	5.76 (2.5 H), 5.71 (2.5 H)	$CDCl_3$
4 + 1.0 equiv of Eu*[e]		10.30 (2.5 H), 9.91 (2.5 H)	7.17, 7.14[d] (5 H)	$CDCl_3$

[a] Iridium complexes exhibit dppe ($-CH_2CH_2-$) and "normal" phenyl resonances as complex multiplets between ~2.0–3.5 (8 H) and ~6.9–9.0 ppm (36 H). [b] Integrations were determined by comparison with total phenyl region (40 H). Each high-field ortho phenyl H resonance (2 or 4 H) is an overlapping doublet of doublets (pseudotriplet) with $^3J_{P-H} \simeq 8$–9 Hz and $^3J_{H-H} \simeq 8$ Hz. [c] Resonances exhibit equal intensity. [d] Ill-resolved shoulder of low-field resonance. [e] ROH* and Eu* represent the chiral solvating alcohol and europium shift reagents.

Table II. ^{31}P NMR Data Chemical Shift (δ) Data[a]

complex	ν_1	ν_2	ν_3	ν_4	$^2J(\nu_{x,y})$, Hz
$[Ir(SO_2)(dppe)_2]^+$	32.3 s				
$[Ir(S_2O)(dppe)_2]^{+\,b,c}$	18.5	10.8	9.0	7.5	$J_{1,2} = 0, J_{1,3} = 10, J_{1,4} = 19\ J_{2,3} = 0, J_{2,4} = 0, J_{3,4} \simeq 3$
$[Ir(S_2O_2)(dppe)_2]^{+\,b,c}$	11.4 pt	10.7 pt			$J_{1,2} \simeq 8$–10^d
$[Ir(Se_2O)(dppe)_2]^{\bullet\,c,e}$	14.1	9.0	9.0	0.7	
$Fe_2Pt(SO)(S)(CO)_6(PPh_3)_2$	16.4 d	13.3 d			$J_{1,2} = 13, {}^1J_{Pt-P_1} = 2946, {}^1J_{Pt-P_2} = 2699$
$Fe_2Pt(SeO)(Se)(CO)_6(PPh_3)_2$	13.4 d	5.3 d			$J_{1,2} = 17$
$Fe_2Pt(TeO)(Te)(CO)_6(PPh_3)_2$	17.4 d	1.6 d			$J_{1,2} = 19, {}^1J_{Pt-P_1} = 3916, {}^1J_{Pt-P_2} = 3640$

[a] d = doublet and pt = pseudotriplet (magnetic nonequivalence present in system). $CDCl_3$ was used unless otherwise stated. [b] In comparison, $[Ir(S_2)(dppe)_2]^+$ exhibits resonances at 21.0 and 18.4 ppm in $CDCl_3$ solution. [c] CH_2Cl_2/CD_3NO_2 (5:1 v/v solvent. [d] Second-order spectrum; estimated value. [e] Peaks are broadened and lack distinct coupling.

and gives $[Ir(S_2O)(dppe)_2]PF_6$ (**1**) in 90% yield. An unexpected feature of the analogous reaction with $[Ir(S_2)(dppe)_2]Cl$ was that up to a 2.5-equiv excess of *m*-CPBA did not convert the $[Ir(S_2O)(dppe)_2]Cl$ to the corresponding S_2O_2 derivative but resulted in decomposition. It is believed that the Cl^- counterion is oxidized under these conditions. In contrast, 2 equiv of *m*-CPBA cleanly converted $[Ir(S_2)(dppe)_2]PF_6$ to $[Ir(S_2O_2)(dppe)_2]PF_6$ (**2**). This system proved to be very sensitive to the nature of the oxidant, and standard reagents such as H_2O_2[17] and *tert*-butyl hydroperoxide[18] reacted slowly with resulting decomposition of the complexes.

^{1}H and ^{31}P NMR spectroscopies were particularly useful in the characterization of **1** and **2**. The ^{1}H NMR spectrum of $[Ir(S_2O)(dppe)_2]^+$ (Table I) consisted of two closely spaced, high-field ortho phenyl proton resonances of equal intensity at 6.40 and 6.46 ppm, characteristic of a *cis*-$[IrXY(dppe)_2]^+$ ($X \neq Y$) species.[19] The ^{31}P NMR spectrum of the S_2O complex is similar to that for $[Ir(S_2CH_3)(dppe)_2]^{2+}$[20] (Table II). The NMR data for both the S_2O and S_2O_2 complexes are consistent with the presence of only a single diastereoisomer although two are possible for **1** and three for **2** (Figure 1). Variable temperature ^{1}H NMR spectroscopy (360 MHz) has not given evidence for dynamic character in **1**. In contrast, we have previously shown that $[Ir(E_2CH_3)(dppe)_2]^{2+}$ (E = S, Se) exists in solution as an NMR-observable equilibrium mixture of two diastereoisomers.[21] The previous synthesis of **1** or **2** required a periodate oxidation,[4,5] which is tedious because of the poor solubility characteristics of IO_4^- salts and the inherent sluggish oxidation rates.[22]

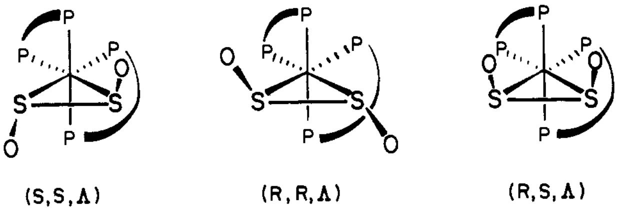
(S,S,Λ) (R,R,Λ) (R,S,Λ)

Figure 1. Coordination sphere and structures for the diastereomers of $[Ir(S_2O_2)(dppe)_2]^+$.

Attempts at oxidation of the green $[Ir(Se_2)(dppe)_2]Cl$ complex with *m*-CPBA led to decomposition even at −60 °C. However, the use of peracetic acid at −10 °C resulted in the rapid formation of orange $[Ir(Se_2O)(dppe)_2]^+$ (**3**). Our previous observation[21] concerning the greater nucleophilicity of diselenium as compared to that of the disulfur ligands is again demonstrated in the facile formation of **3** and parallels similar results for rates of oxidation in organic disulfides and diselenides.[23] The elemental analysis and spectroscopic results of **3** are completely consistent with the presence of an η^2-Se_2O entity. The IR spectrum showed a single ν_{SeO} at 828 cm^{-1},[24] and the ^{1}H NMR spectrum revealed two high-field ortho phenyl proton resonances at 6.28 and 6.76 ppm, which are similar to the results obtained for $[Ir(S_2O)(dppe)_2]^+$. Attempts

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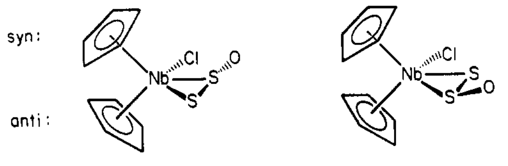


4A **4B**

Figure 2. Two possible diastereomeric structures for $Cp_2Nb(S_2O)Cl$.

at further oxidation of the η^2-Se_2O ligand to η^2-Se_2O_2, even with the PF_6^- counterion present, have not yielded a stable complex. In marked contrast to the η^2-S_2O and η^2-S_2O_2 complexes, $[Ir(Se_2O)(dppe)_2]^+$ is unstable in chloroform solution at 25 °C wherein it completely reverts back to $[Ir(Se_2)(dppe)_2]^+$ after several days. These results demonstrate the significantly greater lability of the Se–O vs. S–O bond in this system and again parallels similar results obtained for organic selenoxides and sulfoxides.[25] Although complex **3** has shown no inclination to react with a variety of substrates (benzylic and allylic alcohols and organic sulfides and disulfides), the oxidation of ethanethiol occurs readily (eq 1).

$$2RSH + [Ir(Se_2O)(dppe)_2]^+ \rightarrow RSSR + [Ir(Se_2)(dppe)_2]^+ + H_2O \quad (1)$$

This parallels the ability of SeO_2 to oxidize thiophenol to phenyl disulfide[10b] and the reaction of trimethyl phosphite with a thermally unstable compound recently identified as an organoselenolseleninate (eq 2).[13] Oxidation of ethanethiol with

$$RSeSe(=O)R' + (CH_3O)_3P \xrightarrow{-50\ °C} RSeSeR' + (CH_3O)_3PO \quad (2)$$

$[Ir(S_2O_2)(dppe)_2]^+$ is very sluggish at 25 °C and does not occur with the S_2O complex under forcing conditions. In general, the S–O units in **2** are inert except toward powerful oxophiles such as phosphines.

Further tests on the generality and versatility of peracid oxidations were conducted with $Cp_2Nb(S_2)Cl$ (Cp = C_5H_5).[26] Addition of peracetic acid to a solution of this complex produced a rapid color change from dark red to light yellow-orange. An 85:15 mixture of $Cp_2Nb(S_2O)Cl$ (**4**) and $Cp_2Nb(O)Cl$ was formed, as determined by ^1H NMR spectroscopy. Attempts to oxidize $Cp_2Nb(S_2O)Cl$ with a second equivalent of peracetic acid led to $Cp_2Nb(O)Cl$ with no evidence for a stable S_2O_2 complex. Compound **4** was purified by silica gel chromatography, and its formula was verified by chemical analysis and the observation of a molecular ion in its field-desorption mass spectrum. It is stable for extended periods as a solid, although complete decomposition to $Cp_2Nb(O)Cl$ and elemental sulfur occurs when solutions of $Cp_2Nb(S_2O)Cl$ are allowed to stand for several days.

The spectroscopic results all indicate the regiospecific formation of a single S_2O complex. A single strong IR absorption at 1020 cm^{-1} is assigned to ν_{SO}. The ^1H and ^{13}C NMR spectra of $Cp_2Nb(S_2O)Cl$ consist of two equally intense singlets that were invariant to 50 °C, which on the basis of the Eyring equation requires $\Delta G^\ddagger > 18$ kcal/mol for inversion at sulfur.[27] Two possible structures for **4** are shown in Figure 2, with **4A** being favored by us on the basis of steric considerations. The geometry proposed for **4** differs from that found crystallographically for $(MeCp)_2Nb(CH_2SiMe_3)(\eta^2\text{-}CO_2)$[28] and $Cp_2Ti(\eta^2\text{-}CH_3CO)Cl$,[29] which contain η^2 ligands, with the exocyclic substituents oriented toward the Cp's.

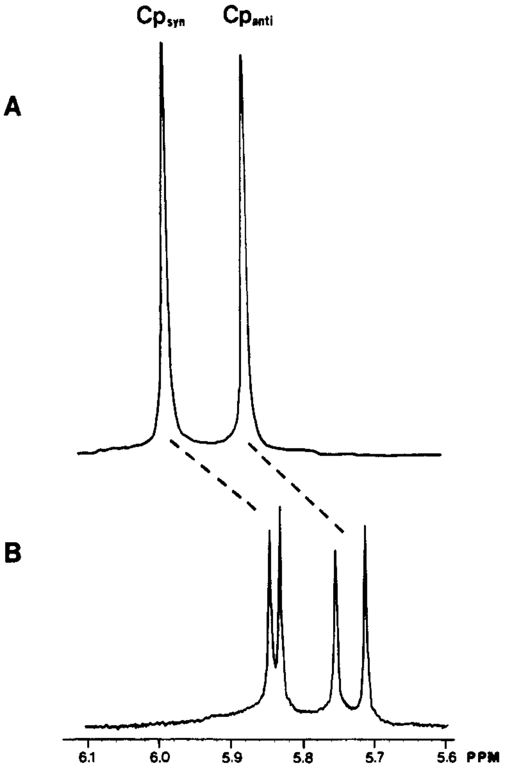
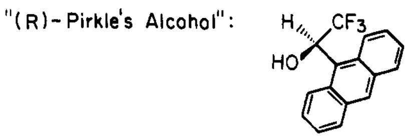


Figure 3. 360-MHz ^1H NMR spectra in $CDCl_3$ of $Cp_2Nb(S_2O)Cl$ (**4**): (A) initial spectrum; (B) spectrum after addition of 6.0 equiv of (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol.



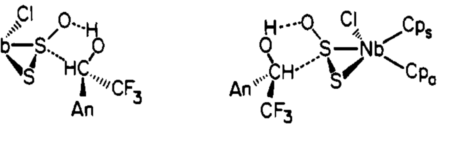
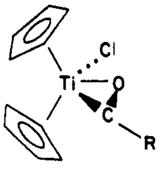
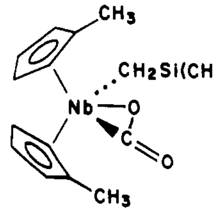


Figure 4. Postulated chelating interactions between (*R*,*S*)-$Cp_2Nb(S_2O)Cl$ and (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol.





It is well-known from organic systems that NMR chemical shifts of functionalities close to sulfoxide groups are sensitive to the presence of aromatic solvents (cf. aromatic solvent induced shifts (ASIS)).[30,31] We observed that both ^1H res-

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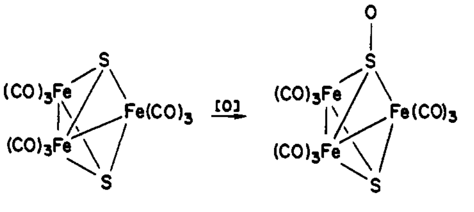
onances for **4** shifted upfield in the presence of a (3:1 v/v) benzene-d_6/$CDCl_3$ solvent mixture compared to the resonances in $CDCl_3$ solution, with the high-field resonance experiencing the greater shielding ($|\Delta\delta| = 0.88$ vs. 0.62 ppm). In ASIS studies on cyclic sulfoxides, the protons adjacent to the sulfur reliably exhibit the largest changes in shifts.[31] This leads us to assign the high field proton signal of **4** to the Cp unit anti with respect to the pyramidal NbS_2O moiety (Table I; structure A in Figure 2).

Corroborative evidence for the stereochemistry of **4** was obtained by using (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol ("Pirkle's alcohol"), which has been used as a diamagnetic chiral solvating reagent (CSA) for organic sulfoxides.[32] We found that 0.3–6.0 equiv of this reagent in a $CDCl_3$ solution of **4** induced upfield shifts and *splitting* of both ^1H signals (Figure 3). The observation that the original high-field (anti) resonance exhibits the largest $\Delta\Delta\delta$ is consistent with the interaction of the shift reagent in the manner shown in Figure 4.[32] A chelating structure is indicated for the solution structure of the anthryl alcohol–**4** complex on the basis of the observation that with the use of the CSA in a (3:1 v/v benzene/chloroform solvent mixture the respective $\Delta\delta$ and $\Delta\Delta\delta$ values for *both* Cp proton resonances are almost equal. This indicates that a competition exists between benzene and Pirkle's alcohol for association at the inner sulfur atom site in **4**. The addition of the chiral paramagnetic shift reagent $Eu(tfc)_3$ to $CDCl_3$ solutions of **4** produced large downfield chemical shift changes for both resonances (Table I), with the magnitude of the shifts comparable to those observed for organic sulfoxides.[33] The low-field resonance, previously assigned to the syn cyclopentadienyl ring, exhibited the greatest $\Delta\delta$ and $\Delta\Delta\delta$ values and split into two completely resolved peaks. Previous work with cyclic organic sulfoxides and europium shift reagents showed the protons spatially closest to the oxygen commonly exhibited the largest $\Delta\delta$ effects, which is in agreement with our previous assignments. All of these results strongly imply that **4** exists as a single diastereomeric compound featuring a nonplanar η^2-S_2O ligand.

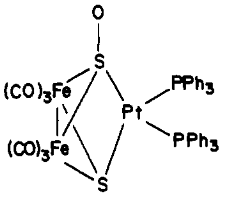
Oxidation of μ_3-E Ligands (E = S, Se, Te). Recently, the first crystallographically characterized transition-metal complex containing a sulfur monoxide ligand, $Fe_3(SO)(S)(CO)_9$ (**5**), was reported.[7] The compound was isolated in 10% yield from the oxidation of $HFe(CO)_4^-$ with a basic aqueous H_2O_2/Na_2SO_3 solution. The X-ray structure revealed a square-pyramidal (nido) cluster with the μ_3-SO ligand capping the triangular Fe_3 core. The close structural similarity between **5** and the well-known complex $Fe_3(S)_2(CO)_9$[34] suggested that a more direct synthetic method should be applicable. Indeed, addition of peracetic acid or *m*-CPBA to a solution of $Fe_3(S)_2(CO)_9$, followed by chromatographic workup, afforded good yields of the desired orange complex **5** (eq 3). The product was identified by elemental analysis and IR spectroscopy, which revealed strong ν_{CO} and ν_{SO} absorptions similar to those previously reported.[7] Attempts at further oxidation of $Fe_3(SO)(S)(CO)_9$ with *m*-CPBA led to decomposition. It is interesting to note that we have found **5** to be an intermediate in the reduction of sulfite by $HFe(CO)_4^-$, leading eventually to $Fe_3(S)_2(CO)_9$.[35]



(3)

5

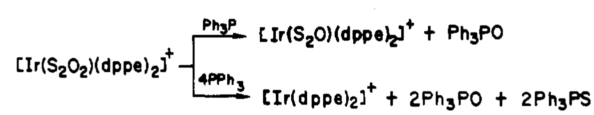
We attempted similar oxidations on a variety of chalcogen-containing organometallic rings and clusters. With one notable exception, these efforts were unsuccessful. $Fe_2(\mu$-$S_2)(CO)_6$, $Co_2(\mu$-$As_2)(CO)_6$, and Cp_2TiS_5 were unaffected by *m*-CPBA, while most (μ_3-S)-containing clusters simply decomposed. However, $Fe_2Pt(S)_2(CO)_6(PPh_3)_2$[36] was cleanly oxidized by *m*-CPBA, affording a good yield of a red crystalline product characterized as $Fe_2Pt(SO)(S)(CO)_6(PPh_3)_2$ (**6**). ^{31}P NMR spectroscopy, one direct structural probe, revealed an AB quartet flanked by the expected ^{195}Pt satellites. The two Pt–P coupling constants, 2946 and 2699 Hz, are appropriate for a cis platinum(II) diphosphine complex.[36,37] Attempts at sulfur or oxygen atom abstraction from **5** and **6** with Ph_3P were unsuccessful, with both complexes remaining inert to chalcogen transfer in solution even at 50 °C for 6 h.



6

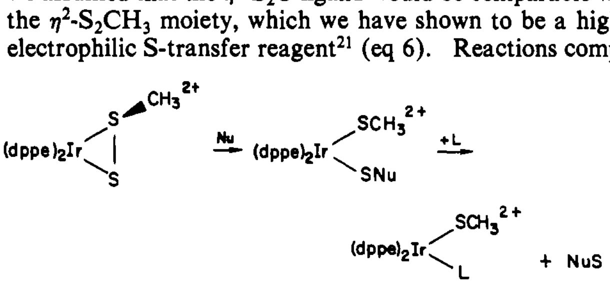
Our experience with $Fe_3(SO)(S)(CO)_9$ and $Fe_2Pt(SO)(S)(CO)_6(PPh_3)_2$ revealed that the latter was more robust thermally. This observation suggested that the other members of the series $Fe_2Pt(EO)(E)(CO)_6(PPh_3)_2$ might also be isolable, whereas oxidation of $Fe_3(E)_2(CO)_9$ (E = Se, Te) complexes led to unstable compounds. Indeed, evidence for the SeO and TeO complexes was obtained by directly following the oxidations with ^{31}P NMR spectroscopy (Table II). $Fe_2Pt(TeO)(Te)(CO)_6(PPh_3)_2$ was readily characterized in solution, although it did undergo decomposition over a period of hours. The corresponding SeO complex was formed as a minor product. No attempts were made to isolate these species.

Attempted Preparation of $[Ir(SO)(dppe)_2]^+$. Schmid et al. have reported the reactions in eq 4 and 5.[4,5] Furthermore, a recent publication describes the related conversion of "$[Rh(SO)X(PPh_3)]_2$" to $RhX(PPh_3)_3$ using PPh_3.[8] However, evidence for simple sulfur monoxide ligands in the rhodium complex remains inconclusive. As a guide in our initial studies, we assumed that the η^2-S_2O ligand would be comparable with the η^2-S_2CH_3 moiety, which we have shown to be a highly electrophilic S-transfer reagent[21] (eq 6). Reactions compa-



$$[Ir(S_2O_2)(dppe)_2]^+ \xrightarrow{Ph_3P} [Ir(S_2O)(dppe)_2]^+ + Ph_3PO \tag{4}$$

$$[Ir(S_2O_2)(dppe)_2]^+ \xrightarrow{4PPh_3} [Ir(dppe)_2]^+ + 2Ph_3PO + 2Ph_3PS \tag{5}$$



(6)

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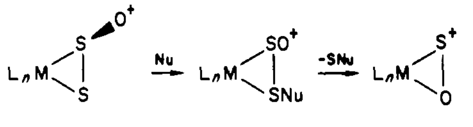
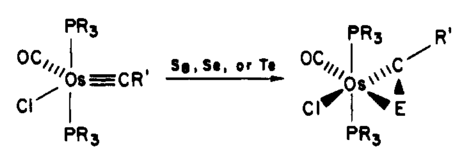
rable to the first step in eq 6 have been observed and reported for the conversion of planar η^2-*SCO*, *SeCS*, and RN*CS* ligands to the corresponding carbonyl, thiocarbonyl, and isocyanide ligands.[38] Following this pathway, the related η^2-S_2O complex could give an η^2-SO complex:


(7)

Two noteworthy features of these reactions are that the unsubstituted, endocyclic chalcogenide atom is the most nucleophilic site and chalcogenide atom transfer is particularly facile for η^2-ECE′ (where E $\neq$ E′). The reverse of this reaction type is exhibited by the addition of chalcogens to Roper's osmium carbyne complex (eq 8).[39]


(8)

In the case of $[Ir(S_2O)(dppe)_2]^+$, the addition of PPh_3 at 25 °C resulted in the formation of Ph_3PS, little Ph_3PO, and no $[Ir(S_2)(dppe)_2]^+$. No evidence supporting the stability of a $[Ir(SO)(dppe)_2]^+$ complex was obtained. Similarly, treatment of $Cp_2Nb(S_2O)Cl$ with even a deficiency of PPh_3 produced only $Cp_2Nb(O)Cl$ and 2 equiv of Ph_3PS. In view of the absence of any Ph_3PO and by assuming the stepwise loss of sulfur from $Cp_2Nb(S_2O)Cl$, we conclude that $Cp_2Nb(SO)Cl$ is formed but is a more active S-transfer reagent than is its precursor. These experiments support the idea that the unsubstituted chalcogenide atom is the most electrophilic site, but isolation of a monometallic η^2-SO ligand apparently requires special stabilizing features.

An attempt was made to synthesize $[Ir(SO)(dppe)_2]^+$ from sulfur monoxide generated in situ. The episulfoxide derivative of *trans*-stilbene is known to thermally eliminate SO concomitant with the formation of the olefin.[40] This reaction has been used in the preparation of "$[RhCl(SO)(PPh_3)_2]_2$",[8] although our results indicate an S_2O complex should be considered. The episulfoxide does not react directly with $[Ir(dppe)_2]^+$ in solution, but upon warming to the decomposition temperature (40 °C) of the episulfoxide, the orange Ir(I) species is rapidly consumed. The principal product is $[Ir(S_2O)(dppe)_2]^+$, as established by ^1H NMR analysis. Under comparable conditions, sulfur monoxide is known to rapidly dimerize to S_2O_2 with subsequent disproportionation to S_2O and SO_2.[41] Thus, it would appear that the rate of addition of SO to $[Ir(dppe)_2]^+$ is significantly slower than the facile autodecomposition of SO.

In view of our inability to isolate complexes containing the η^2-SO ligand, it might be argued that heterodichalcogenide ligands are inherently unstable. We have proven this not to be the case. Previously, we showed that Cp_2TiSe_5 rapidly reacts with $[Ir(dppe)_2]Cl$, giving the Se_2 complex.[42] By employing $Cp_2TiS_xSe_{5-x}$ ($x \approx 2$)[43] as a chalcogen source, we have prepared a mixture of S_2, Se_2, and SSe complexes from $[Ir(dppe)_2]Cl$. While we have not been able to obtain $[Ir(SSe)(dppe)_2]Cl$ (**7**) in pure form by fractional crystallization, both ^1H NMR (Figure 5) and field-desorption mass spectrometry provide unequivocal proof of its existence as a stable molecular entity. A FD-MS of a 1:1 mixture of the iridium S_2 and Se_2 complexes showed molecular ions *only* for those two species, thereby eliminating the possibility that significant quantities of **7** were formed in the probe. Our results indicate other η^2-SSe complexes should also be stable.

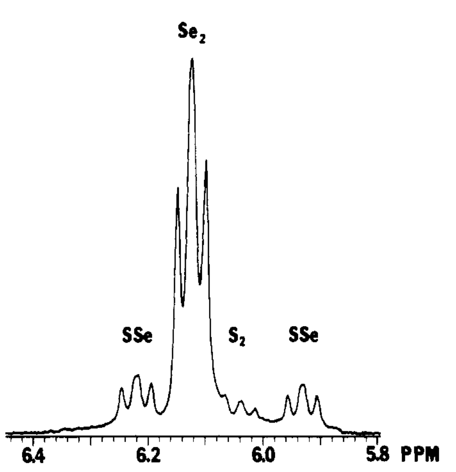
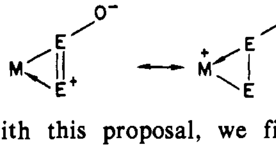


Figure 5. 360-MHz ^1H NMR spectrum (high-field ortho phenyl proton region) of the mixture $[Ir(EE')(dppe)_2]^+$ with EE′ = SSe, Se_2, and S_2.

Summary

This work has established the utility of organic peracids for the oxidation of μ_3-E (E = S, Se, Te) and η^2-E_2 (E = S, Se) ligands. These results complement the findings of the Deutsch[17] and Sargeson groups,[46] who have prepared a variety of cobalt(III) complexes of organosulfur oxides by hydrogen peroxide oxidations. In our studies successful peracid oxidation occurred only for those chalcogen complexes conforming to the EAN rule. This is most evident in the nonoxidizability of the 16-e complex Cp_2TiS_5, which contrasts with the facility of the oxidation of $Cp_2Nb(S_2)Cl$.

The kinetic inertness of the S_2O complexes permitted examination of the ligand-centered reactivity. Reactions of $[Ir(S_2O)(dppe)_2]Cl$ and $Cp_2Nb(S_2O)Cl$ with Ph_3P indicate that the unsubstituted sulfur is the most electrophilic site on the ligands. This polarization may explain why the E_2O (E = S, Se) species prepared in this work do not function as oxygen atom transfer agents. In fact these E_2O complexes closely resemble the corresponding $[Ir(\eta^2\text{-}E_2CH_3)(dppe)_2]^{2+}$ species described earlier.[21] The S_2CH_3 complex proved to be a highly electrophilic S atom transfer agent. These and other results indicate that the charge distribution in η^2-cumulene ligands follows from the resonance forms



Consistent with this proposal, we find that $[Ir(S_2O)$-

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(dppe)$_2$]PF$_6$ undergoes facile O-methylation giving [Ir(S_2OCH_3)(dppe)$_2$]$^{2+}$(PF_6)$_2$, which has been characterized by single-crystal X-ray diffraction. The latter undergoes desulfurization concomitant with CH_3NC coordination affording a stable complex of $SOCH_3$, a close relative of an η^1-SO ligand.[48]

Experimental Section

All standard ^{1}H and ^{13}C{^{1}H}NMR spectra were obtained (at 360 and 90.5 MHz, respectively), as indicated, on a Nicolet NT-360 spectrometer using internal references at 20 °C. ^{31}P{^{1}H} NMR spectra were obtained (at 40.5 MHz) on a modified Varian XL-100 spectrometer at 30 °C using an external D_2O lock with 85% H_3PO_4 as an external reference (downfield shifts positive). IR spectra were obtained with KBr disks on a Perkin-Elmer 599B spectrophotometer. UV–vis spectra were recorded with a Varian Cary 219 spectrophotometer. Field-desorption mass spectra were run on a Varian 731 spectrometer by Carter Cook. Microanalyses were performed by our School of Chemical Sciences analytical laboratory.

All reactions involving Ir(I) or Pt(0) compounds were performed under nitrogen. Reagent grade solvents and commercially available deuterated solvents were used, as indicated. CH_2Cl_2 was distilled from P_4O_{10} under nitrogen. The deuterated solvents were dried over 3-Å molecular sieves and sparged with nitrogen when used as reaction solvents for air-sensitive compounds. For product workup, the solvents were anhydrous when purchased or were dried over 3-Å molecular sieves. Counterion metathesis on products with BF_4^- or PF_6^- was performed by a method previously described.[21] Chromatography was performed by using Bio-Beads S-X4 with CH_2Cl_2 eluent[21] or with 32–63 μm Woelm silica gel that was deactivated by exposing it to atmospheric moisture overnight. 3-Chloroperbenzoic acid (*m*-CPBA), 40% peracetic acid, SO_2(g), tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) (Eu(tfc)$_3$), and (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol with rotation of $[\alpha]^{29}_{D}$ −29.8° (*c* 6.04, $CHCl_3$) were purchased commercially. Iodometric titrations of the peracids were conducted to determine the amount of active oxygen present, with the weights and molar amounts listed in the preparative section corresponding to the amount of pure peracid added. [Ir(E_2)(dppe)$_2$]Cl (E = S, Se),[42,43] (C_5H_5)$_2$Nb(S_2)Cl,[26] $Fe_2Pt(E)_2(CO)_6(PPh_3)_2$ (E = S, Se, Te),[36] $Fe_3(S)_2(CO)_9$,[44] and $Ph_2(CH_2)_2SO$[31,45] are described in the literature.

[Ir(S_2O)(dppe)$_2$]PF$_6$ (1). To a rapidly stirred, cold CH_2Cl_2 solution (0 °C, ~50 mL) of [Ir(S_2)(dppe)$_2$]PF$_6$ (0.60 g, 0.50 mmol) was slowly added dropwise a CH_2Cl_2 solution (15 mL) of *m*-CPBA (95 mg, 0.55 mmol). The reaction mixture quickly changed from an orange to a yellow color. The solvent was removed under vacuum and the solids were slurried with about 15 mL of CH_3OH. The product was recovered by suction filtration and washed several times with small amounts of cold CH_3OH. After the product was dried in vacuo at 40 °C for 1 day, a 90% yield (0.55 g) of light yellow powder was realized. The complex is stable for extended periods as a solid, and thermal decomposition in solution commences at ~80 °C. Anal. Calcd for $C_{52}H_{48}F_6IrOP_5S_2$: C, 51.44; H, 3.99; P, 12.76; S, 5.28. Found: C, 51.05; H, 3.79; P, 12.85; S, 5.43. IR analysis showed a single ν_{SO} band with no evidence for overoxidation to the S_2O_2 complex.

[Ir(S_2O_2)(dppe)$_2$]PF$_6$ (2). To a stirred solution of [Ir(S_2)(dppe)$_2$]PF$_6$ (0.32 g, 0.27 mmol) in CH_2Cl_2 (50 mL) was added a CH_2Cl_2 (20 mL) solution of *m*-CPBA (0.14 g, 0.81 mmol). The reaction mixture quickly changed from an orange to a yellow color, and the color deepened further over a 30-min period. The solvent was removed on a rotary evaporator, and a standard counterion metathesis with NH_4PF_6 was performed. The solids were recrystallized from CH_2Cl_2/diethyl ether, and yellow microcrystals were recovered by suction filtration. After the product was dried in vacuo, a 75% yield (0.24 g) was realized. Anal. Calcd for $C_{52}H_{48}F_6IrO_2P_5S_2$: C, 50.77; H, 3.93; P, 12.59; S, 5.21. Found: C, 50.47; H, 3.87; P, 12.50; S, 5.37. Very slow decomposition (weeks) of the complex was observed both as a solid and in solution, with low yields (~25%) of [Ir(S_2O)(dppe)$_2$]$^+$ produced.

Attempts at an analogous oxidation of [Ir(S_2)(dppe)$_2$]Cl using 2.0–2.5 equiv of *m*-CPBA produced *only* the S_2O complex with yields diminishing as the amount of *m*-CPBA increased.

Table III. Electronic and Infrared Spectral Data

complex	electronic data (325–800 nm),[a] nm	infrared data,[c] cm^{-1}
[Ir(S_2O)(dppe)$_2$]$^+$	362[b]	ν_{SO} = 1049 (s)[d,e]
[Ir(S_2O_2)(dppe)$_2$]$^+$	342	ν_{SO} = 1045 (s), 1019 (s)[d]
[Ir(Se_2O)(dppe)$_2$]$^+$	460, 390, 326	ν_{SeO} = 828 (s)
$Cp_2Nb(S_2O)Cl$	454 (830), 346	ν_{SO} ≃ 1020 (s)[f]
$Fe_2Pt(SO)(S)(CO)_6(PPh_3)_2$	348	ν_{SO} = 1058 (m)
$Fe_3(SO)(S)(CO)_9$	440, 353	[g]

[a] CH_2Cl_2 solvent. Adsorptions usually are shoulders of large UV bands with true ε values not readily obtained. [b] ε ≃ 5300 M^{-1} cm^{-1}. [c] In Nujol, unless otherwise indicated. [d] Values show some variation between samples, possibly concentration dependent. [e] Thin film. [f] Overlaps C–H (in-plane) deformation of Cp absorption band. [g] ν_{SO} and ν_{CO} values comparable to literature values.[7]

[Ir(Se_2O)(dppe)$_2$]PF$_6$ (3). A CH_2Cl_2 solution of peracetic acid (0.4 M) was added dropwise to a stirred CH_2Cl_2 solution (25 mL) of [Ir(Se_2)(dppe)$_2$]PF$_6$ (0.67 g, 0.52 mmol) at −10 °C under N_2. Additon of the peracid was continued until the solution changed from green to light yellow. The solution was concentrated in vacuo and then diluted with Et_2O (35 mL). The solids that precipitated were washed with Et_2O and recrystallized from CH_2Cl_2 solution. The compound was recovered by suction filtration and dried in vacuo. An 80% yield (0.56 g) of yellow-orange powder was realized. Anal. Calcd for $C_{52}H_{48}F_6IrOP_5Se_2$: C, 47.74; H, 3.70; P, 11.84. Found: C, 47.20; H, 3.94; P, 12.27. In chloroform solution, slow reversion to the green [Ir(Se_2)(dppe)$_2$]PF$_6$ complex was observed. As a solid, the complex undergoes very slow decomposition.

An analogous procedure using [Ir(Se_2)(dppe)$_2$]Cl, followed by BF_4^- metathesis, gave similar results. IR data for the BF_4^- salt is listed in Table III.

[Ir(SO_2)(dppe)$_2$]PF$_6$. [Ir(dppe)$_2$]PF$_6$ (36 mg) was dissolved in 2.5 mL of $CDCl_3$ in an N_2-flushed 12-mm NMR tube. The solution was saturated with SO_2(g), which induced a rapid color change from orange to yellow. The product was analyzed by ^{31}P NMR spectroscopy. Similar techniques with a 5-mm tube were used in the ^{1}H NMR studies. The SO_2 ligand is very labile since sparging the solution with N_2 or evaporation of the solvent results in recovery of [Ir(dppe)$_2$]PF$_6$.

Reaction of [Ir(Se_2O)(dppe)$_2$]PF$_6$ and CH_3CH_2SH. To a solution of [Ir(Se_2O)(dppe)$_2$]PF$_6$ (5.0 mg, 3.8 μmol) in CH_2Cl_2 (2 mL) was added ethanethiol (1.1 μL, 15 μmol). The solution was allowed to react for 8 h at 25 °C. After several hours, a green coloration from the [Ir(Se_2)(dppe)$_2$]$^+$ product was apparent. The reaction mixture was analyzed by 360-MHz ^{1}H NMR spectroscopy, which revealed the presence of ethyl disulfide and residual ethanethiol in approximately an equimolar ratio.

(C_5H_5)$_2$Nb(S_2O)Cl (4). To a stirred solution of (C_5H_5)$_2$Nb(S_2)Cl (0.10 g, 0.31 mmol) in CH_2Cl_2 (40 mL) was added dropwise 15 mL of a CH_2Cl_2 solution containing a slight molar excess of peracetic acid. The solution quickly turned from a dark red-brown to a light yellow-orange color. The solution was concentrated to about 15 mL and then diluted with hexanes (30 mL); further concentration to ~15 mL precipitated the crude product. ^{1}H NMR spectroscopy (90 MHz) indicated a mixture of 85% $Cp_2Nb(S_2O)Cl$ and 15% $Cp_2Nb(O)Cl$ was present. The solids were redissolved in a minimum of CH_2Cl_2 and purified by silica gel flash chromatography (10-cm column) with 9:1 CH_2Cl_2/acetone eluent. The yellow band that slowly eluted was collected and the solvent evaporated to dryness. A 52% yield (56 mg) of yellow-orange powder was obtained. IR (Nujol): ν_{SO} = ~1029 (s) cm^{-1} and ν_{MS_2} = 520 cm^{-1}. Anal. Calcd for $C_{10}H_{10}ClNbOS_2$: C, 35.46; H, 2.98; S, 18.93; Cl, 10.47. Found: C, 35.52; H, 3.08; S, 18.76; Cl, 10.34. FD-MS: *m/e* (%) 338 (100, M$^+$) and 326 (19, M$^+$ − S). In solution, the product will decompose after several days to $Cp_2Nb(O)Cl$ and elemental sulfur. The purity of the $Cp_2Nb(S_2O)Cl$ can be easily determined by ^{1}H NMR spectroscopy or silica gel TLC. ^{13}C NMR ($CDCl_3$): δ 111.3 (s) and 115.3 (s).

$Fe_3(SO)(S)(CO)_9$ (5). To a stirred solution of $Fe_3(S)_2(CO)_9$ (0.10 g, 0.21 mmol) in CH_2Cl_2 (25 mL) was added dropwise a solution of 40% peracetic acid (3.0 mmol) in CH_2Cl_2 (0.5 mL). Progress of the reaction was followed by silica gel TLC with benzene eluent. The reaction mixture was successively washed with saturated aqueous

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$NaHCO_3$ solution, 5% w/v aqueous $NaHCO_3$ solution, and then water. Finally, the organic layer was dried over Na_2SO_4 and decanted, and the solvent was removed on a rotary evaporator. A yield of 69% (71 mg) of the dark purple microcrystals was realized. The identity and purity of the complex was verified by comparison of the IR and silica gel TLC results with those of an independently prepared sample.

$Fe_2Pt(SO)S(CO)_6(PPh_3)_2$ (6). A mixture of $Fe_2(S_2)(CO)_6$ (0.14 g, 0.41 mmol) and $Pt(PPh_3)_2(C_2H_4)$ (0.31 g, 0.41 mmol) was dissolved with CH_2Cl_2 (50 mL). The reaction mixture was stirred for 10 min, and then *m*-chloroperoxybenzoic acid (0.20 g, 1.2 mmol) was added. The red color of the reaction mixture darkened, and the solution was allowed to stir for 30 min. The solution was washed with saturated aqueous $NaHCO_3$ solution (3 × 100 mL) and then 100 mL of H_2O. The organic layer was dried over Na_2SO_4, and solids were removed via filtration. Hexanes were added to the filtrate, and the solution was concentrated to a small volume on a rotary evaporator. The product was isolated by filtration and washed with hexanes. After the product was dried in vacuo, a 62% yield (0.27 g) of red crystals was obtained. Anal. Calcd for $C_{42}H_{30}Fe_2O_7P_2PtS_2$: C, 46.72; H, 2.80; P, 5.74; S, 5.94. Found: C, 46.62; H, 2.79; P, 5.53; S, 5.86. FD-MS: *m/e* 1080 (M^+).

$[Ir(SSe)(dppe)_2]Cl$ (7). A mixture of $[Ir(dppe)_2]Cl$ (50 mg, 49 μmol) and $(MeCp)_2TiS_xSe_{5-x}$ ($x \approx 2$; 25 mg, ~50 μmol) was dissolved with 1,2-dichloroethane (20 mL). The reaction mixture was stirred for 20 min, and then the solvent was evaporated in vacuo. The solids were redissolved in CH_2Cl_2, and the iridium-containing products were isolated by gel permeation chromatography on Bio-Beads S-X4 with CH_2Cl_2 elution. The green fraction, which eluted first, was collected and the solvent removed under vacuum. ^1H NMR (360 MHz) spectroscopy indicated a mixture of products with cis stereochemistry comprised of 17% $[Ir(SSe)(dppe)_2]^+$, 75% $[Ir(Se_2)(dppe)_2]^+$, and 6% $[Ir(S_2)(dppe)_2]^+$. FD-MS for the SSe complex: *m/e* 1101 (M^+), with the signal intensities of the isotopic cluster closely matching a computer-simulated pattern. Attempts at fractional crystallization of pure $[Ir(SSe)(dppe)_2]^+$ from the product mixture were not successful.

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Registry No. **1**, 63627-91-8; **2**, 91602-15-2; **3**, 91467-39-9; **4**, 91467-40-2; **5**, 73137-67-4; **6**, 91491-47-3; **7**, 91467-41-3; *m*-CPBA, 937-14-4; $[Ir(S_2)(dppe)_2]PF_6$, 91467-43-5; $[Ir(S_2)(dppe)_2]Cl$, 31603-13-1; $[Ir(Se_2)(dppe)_2]PF_6$, 91548-31-1; $[IrSe_2(dppe)_2]Cl$, 40603-51-8; $[Ir(dppe)_2]PF_6$, 41047-09-0; $(C_5H_5)_2Nb(S_2)Cl$, 72478-51-4; $Cp_2Nb(O)Cl$, 59412-84-9; $Fe_3(S)_2(CO)_9$, 22309-04-2; $Fe_2(S_2)(CO)_6$, 14243-23-3; $Pt(PPh_3)_2(C_2H_4)$, 12120-15-9; Se_2, 12185-17-0; S_2, 23550-45-0; CH_3CH_2SH, 75-08-1; peracetic acid, 79-21-0.

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Polarized Neutron Diffraction and Mössbauer-Effect Study of the Magnetic Ordering in Wüstite, Fe_yO

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Samples of nonstoichiometric iron(II) oxide, Fe_yO, have been studied by polarized neutron diffraction, at 45 K, and Mössbauer spectroscopy, at 4.2 and 78 K. The neutron measurements, on samples of compositions $Fe_{0.926}O$ and $Fe_{0.943}O$, show that antiferromagnetic order is maintained in the vicinity of defect clusters. In the intercluster region the spin direction is approximately 30° from [111], but close to the defects it is about 35° from the (111) plane. The spin structure is approximately collinear at the local level. The Mössbauer spectra of a sample of composition $Fe_{0.918}O$ are extremely complex. They have been fitted to a model involving one iron(III) hyperfine sextet, two iron(II) hyperfine sextets, and an iron(III) quadrupole doublet with a very large splitting (3.8 mm s^{-1}). The doublet is ascribed to the iron(III) tetrahedral interstitials, which may be paramagnetic or spin paired with adjacent interstitials.

Introduction

Nonstoichiometric wüstite, Fe_yO, adopts the rock salt structure above its magnetic-ordering temperature. The deficienty of iron is accommodated by octahedral iron vacancies that are associated with tetrahedral interstitials to form clusters.[1] The simplest defect cluster is the 4:1 unit, containing four octahedral iron vacancies around a single tetrahedral interstitial (Figure 1a)), but X-ray and neutron diffraction measurements of the vacancy: interstitial ratio point to more extended aggregates.[2-5] Theoretical calculations favor edge-shared clusters such as the 6:2 (Figure 1b) and 8:3 units.[6] The creation of iron vacancies in iron(II) oxide is, of course, accompanied by the formation of iron(III), and in order to balance the charge locally, the iron(III) is thought to be located at the interstitial positions and in the immediate vicinity of the clusters.[6] A surprising feature of the 6:2 and related moieties is that the Fe(III)–Fe(III) distance between adjacent tetrhedral interstitials is very short (ca. 2.1 Å) and is certainly in the range where appreciable metal–metal interaction would seem likely.

The bulk magnetic properties of wüstite are well-known and indicate that it is antiferromagnetic below ca. 195 K, with the exact Nêel temperature depending upon y.[7] Neutron diffraction measurements obtained below T_N show that it undergoes a rhombohedral distortion ($\alpha < 60°$) and that the bulk of the iron spins are aligned along the [111] axis of the cell; α increases with decreasing y.[1] Alternate (111) sheets are ferromagnetic and have α and β spins, respectively. A re-

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