THE COORDINATION CHEMISTRY OF SULFOXIDES WITH TRANSITION METALS

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I. Introduction

Interest in the coordination chemistry of sulfoxides has stemmed primarily from the excellent solvent action of the lower sulfoxides. Several review articles have appeared which discuss various aspects of the inorganic chemistry of sulfoxides (Table I), but these deal almost exclusively with the chemistry of dimethyl sulfoxide alone. Interest in the inorganic chemistry of the higher sulfoxides has recently developed as a result of much research into the use of sulfoxides in the solvent extraction of metals during refining processes; specific details of this applied subject are considered outside the scope of this review, although key references are given where appropriate. Since the early recognition that sulfoxides are capable of acting as Lewis bases (*278*), the coordination chemistry of these interesting ligands remained largely unexplored until a renaissance period began in the early 1960s (*127–129, 162*). During this period it was recognized that sulfoxides are capable of acting as ambidentate ligands, coordinating to specific metals via either oxygen (*O*-) or sulfur (*S*-). The qualitative observation at this time was that dimethyl sulfoxide coordinated to "hard" metals via oxygen and to "soft" metals via sulfur. A comprehensive review of the coordination chemistry of dimethyl sulfoxide appeared shortly after this period (*460*) which supports these observations, but investigation into the use of higher sulfoxides as ligands has shown

TABLE I

REVIEW ARTICLES ON ASPECTS OF SULFOXIDE CHEMISTRY

Subject	Authors (language)
Acid–base strength in Me_2SO	Kolthoff and Reddy (*330*) (English)
The chemistry of Me_2SO (general)	Hsu (*281*) (Chinese)
Coordination compounds of sulfoxides	Gopalakrishnan and Patel (*229*) (English)
The chemistry of Me_2SO (inorganic)	Reynolds (*460*) (English)
The chemistry of Me_2SO (general)	Jacob *et al.* (*296*) (English)
Cis and trans effects in R_2SO complexes	Kukushkin (*340*) (English) and (*342*) (Russian)
Me_2SO as solvent and ligand in inorganic chemistry	Tenhunen (*485*) (Finnish)
Biologically active thioethers and derivatives (including sulfoxides)	Griesser *et al.* (*237*) (English)
The chemistry of Me_2SO (general)	Hauthal and Martin (*269*) (German) and (*270*) (English)
Complex compounds of sulfoxides	Kukushkin (*341*) (Russian)
Deoxygenation reactions of sulfoxides	Drabowicz *et al.* (*160*) (English)

that other factors are also important in determining the mode of coordination. Additionally, advances have been made leading to the isolation of new transition-metal complexes of sulfoxides which have found application as reactive intermediates in preparative coordination chemistry and homogeneous catalysis. The bioinorganic chemistry of sulfoxides has also developed during this period.

This review is intended as an account of the coordination chemistry of both dimethyl sulfoxide and the higher sulfoxides, with particular reference to the mode of bonding and the extent to which this affects the chemistry of transition-metal sulfoxide complexes. No attempt has been made to provide an exhaustive listing of all known sulfoxide complexes, many of which contain coordinated sulfoxide moieties only coincidentally to their other important functions.

NOMENCLATURE

An oxygen-bonded sulfoxide complex will be termed an O-R_2SO complex, and similarly, a sulfur-bonded complex will be termed an S-R_2SO complex. Where the mode of coordination is not known or is uncertain, formulas of the type $[M(R_2SO)_xCl_y]$ will be used.

The following abbreviations will be used throughout the text: L, neutral ligand; X, anionic ligand or uncoordinated anion; R, alkyl or aryl group; Me, CH_3—; Et, CH_3CH_2—; *n*Pr, $CH_3CH_2CH_2$—; *i*Pr, $CH_3C(CH_3)H$—; *n*Bu, $CH_3(CH_2)_3$—; Ph, C_6H_5—; dien, $H_2NCH_2CH_2N(H)CH_2CH_2NH_2$; and acac, $CH_3C(O)CHC(O)CH_3^-$.

II. Physical Studies of Sulfoxide Complexes

In order to understand the bonding in transition-metal sulfoxide complexes, it is necessary to summarize the physical data available in the literature and so determine what constraints are necessary in any bonding model. An understanding of the factors affecting the bonding in these complexes is essential if further developments are to be made in the chemistry of transition-metal sulfoxide complexes.

A. STRUCTURAL STUDIES

The molecular structure of dimethyl sulfoxide has been determined both in the gas phase and in the solid state (Table II). The bond angles suggest that the molecule is approximately pyramidal, with sulfur at the apex. The distortions from the expected pyramidal bond angles are

TABLE II

STRUCTURAL DATA OF DIMETHYL SULFOXIDE

	Bond lengths (Å)			Bond angles (deg)			
State	S—O	C—S	C—H	C—$\hat{\mathrm{S}}$—C	C—$\hat{\mathrm{S}}$—O	S—$\hat{\mathrm{C}}$—H	Reference
Gaseous	1.47	1.82	1.08	100 ± 5	107 ± 5	—	*51*
Gaseous	1.477	1.810	1.095	96°23′	106°43′	107°31′	*494*
Solid (+5°C)	1.531	1.821	1.06–1.10	97.4	106.8	109–111	*176*
		1.775			106.7		
Solid (−60°C)	1.471	1.812	—	97.86	107.04	—	*321*
		1.801			107.43		

explicable on simple repulsion considerations; thus a lone-pair on sulfur and some double-bond character in the S—O bond would lead to C—$\hat{\mathrm{S}}$—O being larger than C—$\hat{\mathrm{S}}$—C, as observed. The double-bond character of the S—O bond is difficult to determine unambiguously from the bond-length data. The structural determination with the highest degree of refinement suggests an S—O bond length of 1.531 Å, but two gas-phase determinations and one other solid-state determination suggest a much shorter bond length, approximately 1.47 Å. The length of a single S—O bond has been estimated as approximately 1.66 Å (*61*), suggesting that the S—O bond in dimethyl sulfoxide does have some double-bond character, although the degree cannot be quantitatively estimated due to the variability of the available data (Table II). The data of Eriks *et al.* (*176*) will be used for comparison purposes, as the data from this determination are better refined and the determination was performed at a temperature closer to the temperatures at which structural determinations of sulfoxide complexes have been performed. Of necessity, any such comparisons of bond-length data should be treated with caution.

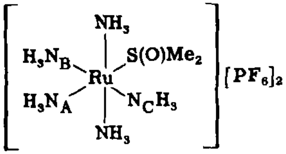
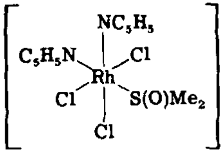
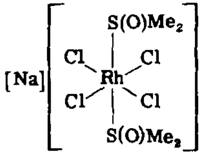
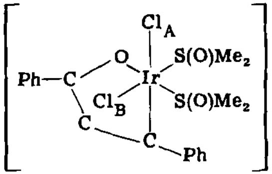
The structural determination of diphenyl sulfoxide has also been performed (*4*), and shows that this diaryl sulfoxide also has an approximately pyramidal structure. The S—O bond length in this molecule is reported as 1.47 Å, again suggesting some double-bond character.

Crystallographic studies on *S*-dimethyl sulfoxide complexes (Table III) show that the geometry of the $\mathrm{Me_2SO}$ moiety is virtually unaffected by coordination. Values of O—$\hat{\mathrm{S}}$—C of ~107° compare favorably with the values of 106.7° and 106.8° reported for free dimethyl sulfoxide. Similarly, reported values of C—$\hat{\mathrm{S}}$—C between 99.4(6)° and 104.5(7)° compare with the value of 97.4° reported for the free molecule. A slight increase in C—$\hat{\mathrm{S}}$—C would be expected on repulsion terms as a result of transfer of electron density from sulfur to the metal (i.e., the repulsive effect of an M—S bond is less than that of the sulfur lone-pair) (see ref. *72* for discussion). Bond-length data show that the C—S distance is also unaffected by coordination; the reported values for *S*-Me_2SO complexes are ~1.8 Å, similar to the values of 1.775 and 1.821 Å reported for the free molecule. The most significant change in the structure of the Me_2SO moiety is the length of the S—O bond. The data shown in Table III clearly show that the S—O bond is shortened relative to the value of 1.531 Å (Table II). The implication of this is that the extent of S—O π-bonding is increased by the transfer of electron density from sulfur to the metal. That the increase in the S—O bond order is a result of extensive π-back-donation of electron density from the metal into an S—O bonding orbital seems unlikely from the structural data available. Thus, in the complex [Ru(*O*-Me_2SO)(*S*-$Me_2SO)_3Cl_2$], the Ru—Cl bond lengths are significantly greater than would be expected for a pure σ-bond (Table IV). This observation suggests that the *trans*-*S*-Me_2SO ligand is not a strong π-acceptor; the presence of a strong π-acceptor trans to a σ-donor would obviously lead to a shortening of the metal–*trans*-ligand bond, and here the converse is observed. The extent of π-back-donation can also be qualitatively estimated from the M—S bond-length data. Thus, in [Ru(*O*-Me_2SO)(*S*-$Me_2SO)_3Cl_2$] (Table IV), the mean Ru—S distance is 2.268 Å, whereas in $[Ru(NH_3)_5$(*S*-$Me_2SO)][PF_6]_2$ (Table III), the Ru—S distance is 2.188(3) Å. The sum of the covalent radii of ruthenium (1.33 Å) and sulfur (1.04 Å) is 2.37 Å, suggesting a slightly lesser degree of π-back-donation in the former compound than in the latter. In the latter complex there are no ligands present which can compete with the *S*-Me_2SO moiety for metal π-electron density, and so these bond lengths follow the expected trend. Similar arguments for K[Pt(*S*-$Me_2SO)Cl_3$] and *cis*-[Pt(*S*-Me_2SO)(*o*-$CH_3 \cdot C_5H_5N)Cl_2$] (Table III) also indicate that the *S*-Me_2SO ligand acts as a poor π-acceptor.

The implications of the structural data for *S*-Me_2SO complexes may be summarized as follows: (*i*) The geometry of the Me_2SO moiety is virtually unaffected by *S*-coordination; (*ii*) the S—O bond order is increased; and (*iii*) the M—S distances suggest that the *S*-Me_2SO ligand is a poor π-acceptor. The structural data for *O*-Me_2SO complexes are shown in Table V. Comparisons with the structural data of free Me_2SO (*176*) are less clear-cut for these complexes, but the bond-angle data show that the geometry of the Me_2SO fragment is little changed upon coordination via oxygen. The value of $M—\hat{O}—S$ (~ 120°) suggests that the geometry about oxygen is effectively "trigonal" (with an oxygen lone-pair occupying the vacant site), and the C—S distances are unaf-

TABLE III

Structural Data of Some *S*-Me_2SO Complexes

Complex	Sum of M + S covalent radii (Å)	Mean bond lengths (Å)			Mean bond angles (deg)				References and notes
		M—S	S—O	S—C	$\mathrm{M{-}\widehat{S}{-}C}$	$\mathrm{M{-}\widehat{S}{-}O}$	$\mathrm{O{-}\widehat{S}{-}C}$	$\mathrm{C{-}\widehat{S}{-}C}$	
	2.37	2.188(3)	1.512(7)	1.815	116.1	114.9(3)	104.2	99.4(6)	*390* $Ru-N_A$ = 2.203(8) $Ru-N_B$ = 2.155(8) $Ru-N_C$ = 2.151(8)
	2.36	2.284(5)	1.48(1)	1.78(2)	111.3	114.7(5)	109.3	99.7(8)	*122*
	2.36	2.29 2.220 2.360	1.47	1.84	—	—	—	—	*234* Environment about S described as distorted tetrahedral
	2.36	2.236	1.45	1.81	111.8	117.3	107	100.5	*392, 393* $Ir-Cl_A$ = 2.496(9) $Ir-Cl_B$ = 2.376(8)

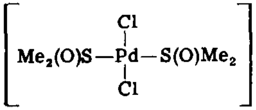
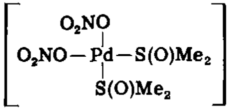
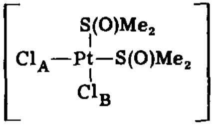
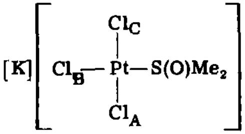
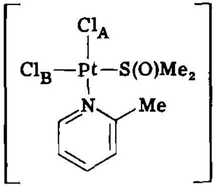
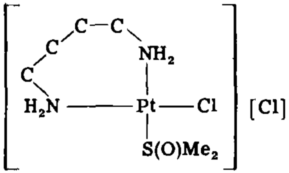
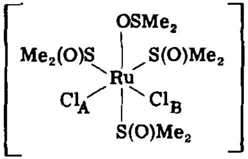
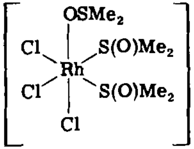
 $[\mathrm{Me_2(O)S{-}PdCl_2{-}S(O)Me_2}]$	2.35	2.299(2)	1.476(2)	1.778	112.3	112.4	109.1	100.9(3)	*61*
 $[\mathrm{(O_2NO)_2Pd(S(O)Me_2)_2}]$	2.35	2.242	1.463(7)	1.789(7)	—	—	—	—	*265*
 $[\mathrm{Cl_ACl_BPt(S(O)Me_2)_2}]$	2.35	2.237	1.462	1.782	111.5	114.8	108.6	101.4	*398* Pt–Cl$_A$ = 2.312(2) Pt–Cl$_B$ = 2.306(3)
 $\mathrm{[K][Cl_ACl_BCl_CPt{-}S(O)Me_2]}$	2.35	2.193(5)	1.476(15)	1.776(16)	11.0(5)	118.3(5)	107.6(7)	102.2(7)	*282* Pt–Cl$_A$ = 2.302(6) Pt–Cl$_B$ = 2.318(5) Pt–Cl$_C$ = 2.296(6)
	2.35	2.200(3)	1.470(9)	1.792	109.4	117.8(4)	107.5	104.5(7)	*399* Pt–Cl$_A$ = 2.288(3) Pt–Cl$_B$ = 2.307(4)
	2.35	2.21(1)	—	—	—	—	—	—	*99* Other lengths and angles are of very low accuracy and are not reported

TABLE IV

STRUCTURAL DATA OF SOME *O*- AND *S*-Me_2SO COMPLEXES

Complex	Sum of M + S covalent radii (Å)	Sum of M + O covalent radii (Å)	Mean bond lengths (Å)				Mean bond angles (deg.)				References and notes
			M—S	M—O	S—O	S—C	$\mathrm{M-\widehat{S}-O}$	$\mathrm{M-\widehat{O}-S}$	$\mathrm{O-\widehat{S}-C}$	$\mathrm{C-\widehat{S}-C}$	
	2.37	—	2.268	—	1.485	1.797	112(2)	—	106.6(6)	99(1)	*400* Ru–Cl_A = 2.435(1)
	—	1.99	—	2.142(3)	1.557(4)	1.788	—	120.0(2)	103(1)	99.0(4)	Ru–Cl_B = 2.435(1)
	2.36	—	2.226	—	—	—	—	—	—	—	*235, 444*
	—	1.98	—	1.990	—	—	—	—	—	—	Other lengths and angles unreported

fected. The S—O bond length is also little changed; some structures suggest a slight increase and others a slight decrease, although those with the highest degree of refinement favor a slight increase in the S—O distance. The M—O bond lengths are long in these complexes, and in no case does the sum of the covalent radii exceed the bond length. The implications of these data may be summarized as follows: (*i*) The geometry of the Me_2SO fragment is virtually unaffected by *O*-coordination; (*ii*) the S—O bond order appears to remain constant or to be slightly decreased; and (*iii*) the M—O bond lengths are long compared with the sum of the covalent radii. Several further points can be derived from the structural data here: the trans influence of the *S*-Me_2SO ligand can be estimated by observing its effect on the length of a *trans*-M—Cl bond. The data in Table VI show that the trans influence of *S*-Me_2SO is approximately equal to that of —NH_2 (or NH_3), and slightly less than that of ethylene. It must be borne in mind that the trans influence is a ground-state effect and only parallels the trans effect of a group where that effect is operative via a σ-mechanism. In cases where a π-induced trans effect is operative (e.g., for CO or ethylene), little or no trans influence will be observed.

The effect of the oxygen atom on the coordinating ability of the sulfur atom in the *S*-Me_2SO group can be assessed by comparing the structure of the thioether complex $[Pt(H_2NCH(COOH)(CH_2)_2SMe)Cl_2]$ (*198*) with that of the sulfoxide derivative (Table VII). The thioether complex has an M—S bond length of 2.26 Å, considerably longer than in the sulfoxide derivative [2.198(2)]. Also, the *trans*-M—Cl distance in the thioether complex is significantly less than in the sulfoxide analog, demonstrating the evaluated trans influence of the *S*-Me_2SO moiety.

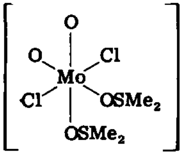
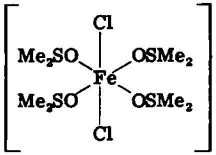
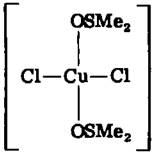
These further points may be summarized as follows: (*i*) the trans influence of *S*-Me_2SO ligands is greater than that of the corresponding thioether; and (*ii*) the M—S bond lengths in sulfoxide complexes are less than those in analogous thioether complexes. The structural data for *S*-R_2SO and *O*-R_2SO complexes ($R \neq Me$) in Tables VII and VIII show that the situation for the higher sulfoxides is analogous to that of Me_2SO. The Pt—Cl bond lengths trans to *S*-R_2SO and trans to olefin may be compared from the data in Table VII and support the hypothesis (*vide infra*) that the trans influences of these ligands are similar in magnitude.

B. VIBRATIONAL SPECTROSCOPIC STUDIES

Early work on sulfoxide complexes (*460*) led to the empirical observation that coordination to a metal center via oxygen generally leads

TABLE V

Structural Data for Some *O*-$\mathrm{Me_2SO}$ Complexes

Complex	Sum of M + O covalent radii (Å)	Mean bond lengths (Å)			Mean bond angles (deg)			References and notes
		M—O	S—O	S—C	$\mathrm{M}{-}\widehat{\mathrm{O}}{-}\mathrm{S}$	$\mathrm{O}{-}\widehat{\mathrm{S}}{-}\mathrm{C}$	$\mathrm{C}{-}\widehat{\mathrm{S}}{-}\mathrm{C}$	
	2.04	2.17	—	—	—	—	—	*194*
 $[\mathrm{FeCl_4}]$	1.86	2.006(6)	1.541(6)	1.800	124.5(4)	103.6	99.4(5)	*59,60*
	1.94	1.955(4)	1.531(4)	1.768	118.2(2)	104.7(3)	100.4(3)	*110,111*
$[\mathrm{Ag}(O\text{-}\mathrm{Me_2SO})_2][\mathrm{ClO_4}]$	2.05	2.358	1.509	1.795	—	105.5	99.7	*80* Infinite chains of Ag atoms linked by bridging $\mathrm{Me_2SO}$ units. Coordination about Ag is distorted trigonal bipyramidal with coordination to perchlorate oxygen

$[HgCl_2]_3[O\text{-}Me_2SO]_2$	1.95	2.54	1.54(1)	1.78(2)	126.0	106	99.9(10)	*79* Structure consists of $[HgCl_2]$ and dimeric $[Me_2SO—HgCl_2]_2$ units linked via Me_2SO bridges
$[La(O\text{-}Me_2SO)_4(NO_3)_3]$	—	2.475	1.50(3)	1.78	—	104	95	*69* Ten-coordinate (each NO_3 group is bidentate) complex
$[Yb(O\text{-}Me_2SO)_3(NO_3)_3]$	—	—	1.45	1.76	—	107.3	102.6	*70* Nine-coordinate (each NO_3 group is bidentate) tricapped trigonal prismatic structure
$[Nd(O\text{-}Me_2SO)_4(NO_3)_3]$	—	2.37	1.51	1.82	137.5	104.1	103.7	*32* Ten-coordinate (each NO_3 group is bidentate) structure; dodecahedron with B-type vertices
$[Er(O\text{-}Me_2SO)_3(NO_3)_3]$	—	2.27	1.57	1.85	129.7	104.8	104.2	*33* Nine-coordinate (each NO_3 group is bidentate) structure; tricapped trigonal prism
$[Lu(O\text{-}Me_2SO)_3(NO_3)_3]$	—	2.26	1.54	1.82	130.8	100.0	101.3	*34, 68* Nine-coordinate (each NO_3 group is bidentate) tricapped trigonal prismatic structure

TABLE VI

INFLUENCE OF TRANS LIGANDS ON M—Cl BOND LENGTHS IN SQUARE-PLANAR Pt(II) COMPLEXES

Complex	Trans atom/ group	M—Cl bond length (Å)	Reference
trans-[Pt(PPhMe$_2$)$_2$(SiPh$_2$Me)Cl]	Si	2.45(1)	*394*
trans-[Pt(PPh$_2$Et)$_2$(H)Cl]	H	2.42(1)	*172*
cis-[Pt(PMe$_3$)$_2$Cl$_2$]	P	2.37(1)	*15*
cis-[Pt(PEt$_3$)(C{OEt}NHC$_6$H$_5$)Cl]	C of carbene	2.365(5)	*36*
cis-[Pt(NH$_3$)$_2$Cl$_2$]	NH$_3$	2.33(1)	*401*
[K][Pt(C$_2$H$_4$)Cl$_3$]·H$_2$O	CH$_2$=CH$_2$	2.327(7)	*310*
[Pt(L-MeSCH$_2$CH$_2$CH{COOH}NH$_2$)Cl$_2$]	S	2.32	*198*
	—NH$_2$	2.31	
cis-[Pt(*S*-Me$_2$SO)$_2$Cl$_2$]	S	2.309(2)	*398*
[K][Pt(*S*-Me$_2$SO)Cl$_3$]	S	2.318(5)	*282*
	Cl	2.299(6)	
[K]$_2$[PtCl$_4$]	Cl	2.308(2)	*380*
cis-[Pt(S{C$_6$H$_4$Cl}$_2$)$_2$Cl$_2$]	S	2.300(4)	*16*
[K][Pt(acac)$_2$Cl$_2$]	O	2.276(5)	*395*
[Pt(*S*-Me$_2$SO)(*o*-CH$_3$NC$_5$H$_5$)Cl$_2$]	S	2.307(4)	*399*
	N	2.288(3)	

to a decrease in the frequency of the band assigned as ν(S=O) (see refs. *13* and *139* for examples), whereas coordination via sulfur generally leads to an increase in frequency (see refs. *87* and *466* for examples). The observation of either bathochromic or hypsochromic shifts (*298*), depending upon the mode of coordination, has proved to be extremely useful to many workers for the assignment of the mode of coordination of sulfoxide ligands; the technique is not, however, infallible, and care must be exercised in its application.

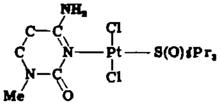
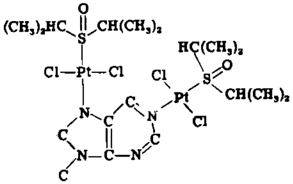
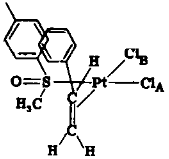
In its infrared spectrum, free Me$_2$SO shows two strong bands in the region where the ν(S=O) mode would be expected, and studies of both Me$_2$SO and its d^6-analog (*195*) have shown that the band at ~1055 cm^{-1} (br) is due largely to ν(S=O) and the band at ~680 cm^{-1} (br) to ν(C—S—C) (sym. and asym.). Upon complex formation, the S—O bond length is affected and a small, but noticeable effect observed on the C—S—C geometry (*vide supra*). The corresponding shifts in the positions of the ν(S=O) and ν(C—S—C) bands can easily lead to errors in the assignment of the two bands (see refs. *128, 129, 132,* and *161* for discussion). To be certain of assigning the correct bands as ν(S=O) and ν(C—S—C), it is advisable to prepare both Me$_2$SO and d^6-Me$_2$SO analogs of a given complex. Comparison of the infrared spectra thus allows unambiguous assignment of both bands (see refs. *180* and *313* for examples).

An additional pitfall is to attempt correlation between the magnitude of the shift in ν(S=O) upon complexation [$\Delta\nu$(S=O)] with the strength of the M—O or M—S bond. The band assigned as ν(S=O) in free Me_2SO is not a pure vibration, and approximately half the potential energy of this vibration is associated with methyl rocking modes (*64*). The use of the magnitude of $\Delta\nu$(S=O) as an estimation of the M—O or M—S bond strength can be seen to be unfounded by considering the infrared spectrum of $[Ru(NH_3)_5(S\text{-}Me_2SO)][PF_6]_2$ (*224*). The position of ν(S=O) at 1045 cm^{-1} shows that coordination has had little effect [$\Delta\nu$(S=O) = 10 cm^{-1}], but the M—S bond length (see Table III) is relatively short and the complex is quite stable. In addition, the position of ν(S=O) represents a decrease in frequency upon coordination, the opposite to that normally observed in *S*-bonding. An explanation based on metal–ligand π-bonding has been proposed (*224*). It has been pointed out (*133*) that any comparisons of $\Delta\nu$(S=O) as a measure of bond strength should take into account the masses of the different metal ions involved, and yet many series have appeared which do not do so. Frequently, complexes of sulfoxides which show little or no change in ν(S=O) upon coordination are reported to contain lattice-held or very weakly bonded molecules of the ligand. For example, $[Th(C_9H_6NO)_4(Me_2SO)_2]$ exhibits $\Delta\nu$(S=O) = −25 cm^{-1} (*3*), and $[CuL_2(Me_2SO)_2]$ (where HL = 7-azaindole) exhibits $\Delta\nu$(S=O) = −35 cm^{-1}, 0 cm^{-1} (*91*). The data described above for $[Ru(NH_3)_5(S\text{-}Me_2SO)][PF_6]_2$ show that this is not always the case. Accordingly, series of M—O and M—S bond strengths derived from values of $\Delta\nu$(S=O) should be treated with caution.

Work on the infrared spectra (500–265 cm^{-1}) of both *O*- and *S*-Me_2SO complexes has shown that ν(M—O) is coupled with $\nu(C—S)_{sym}$, δ(C—S—O) and δ(C—S—C). The ν(M—S) mode is also strongly coupled with internal ligand vibrations, making differentiation between *O*- and *S*-bonding by identification of ν(M—O) or ν(M—S) extremely difficult (*312*). A further problem in using the infrared spectra of sulfoxide complexes to determine the mode of coordination can arise if other strong vibrations due to the molecule are present in the ν(S=O) region, either obscuring or occurring close to, the ν(S=O) mode. Thus, the reported complex $[Pd(dien)(S\text{-}Me_2SO)][ClO_4]_2$ has the ν(S=O) region obscured by the intense ν_3 vibration of the perchlorate anion, making assignment by this technique impossible (*116*). This limitation may be overcome in some instances by suitable modification of the molecule. Thus, preparation of both $[Pd(Ph_2PCH_2CH_2PPh_2)(O\text{-}Me_2SO)Cl][X]$ (X = ClO_4, PF_6) complexes (*143*) allowed inspection of the entire ν(S=O) region as the perchlorate anion absorbs at ~1100 cm^{-1} and the hexafluorophosphate at ~830 cm^{-1}. The presence

TABLE VII

Structural Data for Some *S*-R$_2$SO (R ≠ Me) Complexes

		Mean bond lengths (Å)		Mean bond angles (deg)	
Complex	Sum of M + S covalent radii (Å)	M—S	S—O	M—$\widehat{\text{S}}$—O	References and notes
	2.35	2.31(2)	1.46(1)	116.0(3)	*376* Example of coordination of Pt–R$_2$SO complexes to DNA-type bases
	2.35	2.24	—	—	*375* Geometry of *i*Pr$_2$SO fragment said to be unaffected by coordination
	2.35	2.252(2)	1.461(5)	—	*42* Phenyl groups of styrene and Ph(Me)SO arranged for attractive interaction Pt–Cl$_A$ = 2.301–2.320 Pt–Cl$_B$ = 2.297–2.308

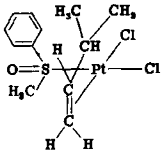
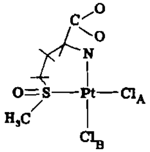
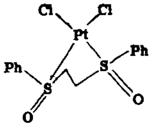
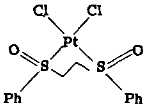
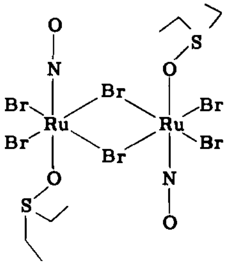
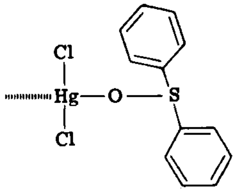
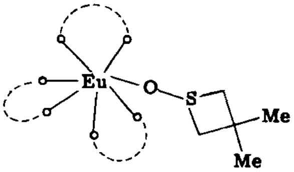
	2.35	2.235(3)	1.466(7)	116.3(3)	*43* Analog of above structure with no possibility of phenyl interaction
	2.35	2.198(2)	1.422(7)	116.1(3)	*199* $Pt-Cl_A = 2.323(2)$ $Pt-Cl_B = 2.304(2)$
	2.35	2.213	1.465	118.9	*24* Complex of meso-$PhS(O)CH_2CH_2S(O)Ph$
	2.35	2.190	1.43	119.8	*25* Complex of rac-$PhS(O)CH_2CH_2S(O)Ph$

TABLE VIII

STRUCTURAL DATA FOR SOME O-R_2SO (R ≠ Me) COMPLEXES

Complex	Sum of M + O covalent radii (Å)	Mean bond lengths (Å)		Mean bond angles (deg)	References and notes
		M—S	S—O	M—O—S	
	1.99	2.050(7)	1.541(7)	123.9(4)	*191*
	1.95	2.58(1)	1.51(1)	—	*78* Further Hg····phenyl interactions give rise to chain-like structure
	—	2.40	—	—	*18* Wedged octahedral structure for 1:1 adduct of tris(dipivalomethanato)europium(III) and 3,3-dimethylthietane-1-oxide

of additional strong bands in the ν(S=O) region can also make assignment difficult. For example, in the complex $[WO_2Cl_2(Me_2SO)_2]$ (*89*), vibrations due to both S—O and W—O appear in the region 890–1050 cm^{-1}. As there is no strong band in the region 1050–1200 cm^{-1} due to S-Me_2SO, this complex as assigned as O-bonded "by default." Similar problems arise in the infrared spectra of $[VOBr_2(R_2SO)_n]$ (R = Me, n = 5; R = Ph, n = 3) (*415*), their chloro analogs (*280*), and other oxo complexes of this type. This problem can also arise in S-R_2SO complexes; for example, $[Pd(S\text{-}Me_2SO)_2(SO_4)]$ (*177*) has an extremely complex ν(S=O) region due to the presence of *cis*-*S*-Me_2SO ligands and a chelating sulfate group. The infrared spectra of higher sulfoxide complexes are generally less informative and often only empirical observations have been made. For example, thiacyclohexane oxide complexes show a series of bands in the ν(S=O) region, and the only definite conclusion that could be made concerning these was that, relative to the free ligand, coordination to a "hard" metal caused a shift to lower frequency (*171*). Also it has been observed (*389*) that aromatic sulfoxides generally exhibit larger values of $\Delta\nu$(S=O) than aliphatic sulfoxides. The problem of multiple bands in the ν(S=O) region of certain sulfoxides has been investigated (*419*), and evidence from variable-temperature infrared studies suggests that rotational isomerism about the C—S bonds may be the cause. It is also noteworthy that the technique of examining shifts in the infrared spectra of sulfoxide complexes can be applied to selenoxide complexes (with similar constraints) to determine the mode of coordination (*311*). The pitfalls in using solely infrared data to determine the mode of coordination of a sulfoxide ligand are exemplified by considering the spectrum of a complex of empirical formula $[Au(Me_2SO)_2(H)Cl_4]$ (*445, 446*). A strong band at 937 cm^{-1}, assigned as ν(S=O) [$\Delta\nu$(S=O) $= -118$ cm^{-1}] may easily be taken as an indication of coordination of Me_2SO via oxygen to the metal center. Application of other analytical techniques in fact defined the complex as $[H(Me_2SO)_2][AuCl_4]$, where the Me_2SO moiety is present solely in the cation, $[H(Me_2SO)_2]^+$, and does not take part in any metal–ligand interaction whatsoever.

In the chemistry of main-group element sulfoxide complexes, a relationship between $\Delta\nu$(S=O) and the enthalpy of formation of the sulfoxide complex has been derived (*159*). The applicability of the equation has only been examined for *O*-R_2SO complexes, and the constraints on using $\Delta\nu$(S=O) as a measure of metal–ligand bond strength should be borne in mind during its application.

C. ^1H NMR STUDIES

Proton NMR studies have proved extremely useful in determining the mode of coordination of sulfoxide ligands. The ^1H NMR spectrum of free Me_2SO exhibits a single resonance, $\delta(CH_3)$ at 2.53 ppm relative to TMS, and the position of this resonance is affected by coordination to a metal center. Only a small effect is observed in *O*-bonding, and generally the value of $\delta(CH_3)$ is increased by 0.5 ppm at the most. Thus, the α-protons of the ligands are scarcely deshielded upon coordination via oxygen. Additionally, where the metal center in a complex has a nonzero-spin (e.g., ^{195}Pt, $I = \frac{1}{2}$, 33.7% natural abundance in the complex $[Pt(Ph_2PCH_2CH_2PPh_2)(O\text{-}Me_2SO)Cl][PF_6]$), observation of M–^{1}H coupling may be expected, but is not seen (*143*). In the case of diethyl sulfoxide, where the methylene protons of the free ligand are inequivalent (*261*), the inequivalence may be reduced by complexation via oxygen (*155*). Complexation via sulfur has a more readily observable effect on the ^{1}H NMR spectra of the ligand. The amount of deshielding of the α-protons is considerable, and shifts of ~1 ppm are commonly observed (e.g., *328*). Additionally, M–^{1}H coupling is frequently evident and for ligands such as Et_2SO, methylene proton inequivalence is increased (*156*). A comparison of the magnitude of the ^{195}Pt–^{1}H coupling constants in $[Pt(S\text{-}Me_2SO)_2Cl_2]$ (*156*) and $[Pt(Me_2S)_2Cl_2]$ (*258*) shows the former to be substantially smaller (23 Hz vs. 49.5 Hz). Other studies (for example, *86*) suggest that $J(^{195}Pt-^1H)$ values of ~20 Hz are typical for simple platinum sulfoxide complexes. This has been taken as an indication of stronger Pt—S σ-bonding in the thioether complex (*156*) than in the sulfoxide complex. It should be borne in mind that the crystallographic data cited above indicate shorter M—S bonds in sulfoxide complexes than in thioether complexes, and that sulfoxides are poor π-acceptors.

The use of both $\delta(CH_3)$ values and $J(M-^1H)$ magnitudes does, however, allow determination of the coordination mode in many instances (e.g., *462*). Problems due to ligand dissociation are frequently evident in ^{1}H-NMR studies of sulfoxide complexes. Thus the dimethyl sulfoxide adduct of niobium oxychloride (*409*) undergoes solvolysis in acetonitrile as in Eq. (1). Similar problems occur in S-Me_2SO complexes also (for example, *314*); accordingly, solvolysis problems limit the scope of the ^{1}H-NMR technique for determination of the coordination mode. Contact-shift and line-broadening studies on $[M(O\text{-}Me_2SO)_6]^{2+}$ species (M = Cu, Ni, Co, Fe, Mn), however, give some indication of the bonding model. Thus, for M = Ni or Cu, unpaired spin density appears to be transferred from L → M via a σ-bonding system, whereas for M = Co, Fe, or Mn, the sign of the electron spin–nuclear spin coupling constant suggests ligand (π) → metal (t_{2g}) unpaired spin density transfer (*414*). Other systems (e.g., $[ML_6]^{3+}$, M = Fe, Cr; L = O-Me_2SO) exchange either too rapidly or too slowly to be investigated by these methods. In summary, the ^{1}H-NMR spectra of O-R_2SO complexes exhibit: (1) small downfield shifts of the α-proton resonance (<0.5 ppm); (2) no $J(M-^1H)$; and (3) reduction of methylene proton inequivalence. Correspondingly, the ^{1}H-NMR spectra of S-R_2SO complexes exhibit: (1) large downfield

$$[NbOCl_3(O\text{—}Me_2SO)_2] \xrightleftharpoons{MeCN} [NbOCl_3(O\text{—}Me_2SO)(MeCN)] + Me_2SO \qquad (1)$$

shifts of the α-proton resonance (~1 ppm); (2) $J(M-{}^1H)$; and (3) increases in methylene proton inequivalence.

D. ELECTRONIC SPECTROSCOPIC STUDIES

The electronic spectra of simple sulfoxide complexes have proved useful in determining the position of sulfoxides in series of ligands ordered by their donor ability as defined by the magnitude of Dq, the ligand field splitting. The results are by no means straightforward; for example, the Dq values of pyridine *N*-oxide are larger than those for Me_2SO and $(CH_2)_4SO$ in $[ML_6]^{n+}$ complexes of Ni(II) and Co(II), but the order is reversed for Cr(III). A simple explanation (*163*) is that the pyridine *N*-oxide ligand has a larger net dipole moment than the sulfoxides and thus exerts a stronger ligand field on the M(II) species. In the case of Cr(III), the highly charged ion would exert a greater polarizing effect and so the more easily polarized sulfoxides would be expected to exhibit the greater splitting.

In terms of a ligand's polarizability or covalent donor ability, the nephelauxetic series is of use for comparative purposes (*318*). A series $O\text{-}Me_2SO \sim O\text{-}(CH_2)_4SO > H_2O > C_5H_5NO$ has been presented (*163*), but other data (*101*) suggest that O-Me_2SO be placed between the N-SCN^- and CN^- ions. A generally accepted series compiled from many results (*319*) is: $I^- > Br^- > CN^- \sim Cl^- > N\text{-}NCS^- > [\text{oxalate}]^{2-} \sim \text{en} > NH_3 > \text{urea} > H_2O > F^-$. As this series is approximately independent of the metal ion in the complex, some discrepancy is apparent.

Other workers have reported reflectance spectra of sulfoxide complexes (for example, *181, 242*), but data are too incomplete to allow meaningful comparisons to be made.

Electronic spectroscopy has been employed to study substitution reactions of sulfoxide complexes. An interesting example (*104*) is the reaction of $[Fe(O\text{-}Me_2SO)_6]^{3+}$ with chloride ion. Addition of one equivalent of chloride ion to a Me_2SO solution of $[Fe(O\text{-}Me_2SO)_6]^{3+}$ causes a change in spectrum, but further additions have no effect. Comparisons with known compounds indicate that $[Fe(O\text{-}Me_2SO)_5Cl]^{2+}$ is the major species in solution.

E. X-RAY ABSORPTION AND EMISSION SPECTROSCOPIC STUDIES

A theoretical correlation between the shift in energies of the sulfur atom K_α and K_β X-ray emission lines and the integral electron density on the sulfur atom of a given sulfoxide has been deduced (*134*), and the number of valence shell electrons on the sulfur atom of free Me_2SO

found to be 5.30 ± 0.08 (*471, 472, 484*). This leads to the deduction that the sulfur atom carries a considerable net positive charge and that the S=O bond is correspondingly polarized in the free molecule. Higher sulfoxides have also been studied, and in all cases the sulfur atom was found to carry a net positive charge, which is almost independent of chain length for dialkyl sulfoxides (*19*). A comparison of the positive charge on the sulfur atoms of both dialkyl and diaryl sulfoxides shows that the latter has a decreased positive charge, while there is evidence of $d_\pi - p_\pi$ interaction in both cases (*373*).

Upon coordination via oxygen, as in uranyl sulfoxide complexes and thorium nitrate sulfoxide complexes, the positive charge on sulfur is virtually unaltered (*19*), whereas coordination via sulfur, as in palladium(II) sulfoxide complexes, causes an increase in the positive charge, as a result of transfer of electron density from the sulfur atom to the metal center (*19, 373*).

To summarize, free sulfoxides carry a net positive charge on the sulfur atom which: (1) is independent of chain length in dialkyl sulfoxides, (2) is greater for dialkyl sulfoxides than diaryl sulfoxides, (3) is virtually unaltered by *O*-bonding, and (4) is increased by *S*-bonding.

F. ESCA STUDIES

Application of electron spectroscopy for chemical analysis (ESCA) to the study of ambidentate sulfoxide coordination has been reported (*184*). The difference between the oxygen 1s and sulfur $2p_{3/2}$ ionization potentials (O1s − S$2p_{3/2}$) appears to be indicative of the mode of coordination, although comparative data are scarce. The complex [Cu(*O*-$Me_2SO)_2Cl_2$] (*O*-bonded, by X-ray crystallography) gives a value of O1s − S$2p_{3/2}$ = 365.7 eV, whereas [Pd(*S*-$Me_2SO)_2Cl_2$] (*S*-bonded, by X-ray crystallography) has O1s − S$2p_{3/2}$ = 365.1 eV. Other compounds, indicated by infrared and ^{1}H-NMR data to be *O*-bonded, suggest that a value of 365.8 eV is typical, whereas a range of compounds assigned as *S*-bonded typically have values of O1s − S$2p_{3/2}$ = 365.0 eV. Of the one cationic and 25 neutral complexes reported in this study, none were mixed neutral-ligand complexes. One such complex has been studied, [Pd($Ph_2PCH_2CH_2PPh_2$)(*O*-$Me_2SO)_2$][$ClO_4]_2$ (*144*), which also gives a typical value of O1s − S$2p_{3/2}$ for an *O*-R_2SO complex (365.7 eV).

The technique, although attractive, is experimentally rather complex; charging problems can frequently occur, leading to the observation of elevated apparent binding energies, and interpretational difficulties exist. Thus, the X-PES of palladium(II) sulfoxide complexes are difficult to interpret unambiguously as the oxygen 1s peak is nearly coincident with the very large palladium $3p_{3/2}$ peak, making accurate assignment difficult (*486*).

G. THERMAL ANALYSIS

Great care must be exercised in the thermal analysis of certain sulfoxide complexes. Complexes of the type $[M(R_2SO)_x][X]_y$ ($X = ClO_4$, NO_3, etc.) are known to be highly explosive on heating to elevated temperatures; indeed, sulfoxide complexes with explosive properties equal to TNT and nitroglycerine have been reported in the patent literature (*148, 149*).

Thermal analysis has proved useful in determining the number of sulfoxide moieties which are lattice-held in a given complex. For example, the thorium and zirconyl perchlorate complexes of Me_2SO undergo thermal degradation [Eqs. (2) and (3)].

$$[Th(Me_2SO)_{12}][ClO_4]_4 \rightarrow [Th(Me_2SO)_6][ClO_4]_4 \qquad (2)$$

$$[ZrO(Me_2SO)_8][ClO_4]_2 \rightarrow [ZrO(Me_2SO)_6][ClO_4]_2 \qquad (3)$$

The "excess" sulfoxide molecules in these complexes were lattice-held and so readily lost on heating (*336*). A tentative suggestion concerning isomerization (O-Me_2SO → S-Me_2SO) was also made for these complexes. Differential thermal analysis of square-planar palladium(II) and platinum(II) sulfoxide complexes has shown trans → cis isomerization for $[M(S\text{-}Me_2SO)(Am)Cl_2]$ ($M = Pd, Pt$; Am = amine such as hydroxylamine, α-, β-, and γ-picolines, etc.) by specific endo- and exothermic effects (*5, 166, 359*). These transformations are further discussed in Section IV,A,3. Studies on the thermal decomposition of $[Pt(en)(L)X][X]$ complexes ($L = R_2S, R_2SO$; R = Me, Et, *n*Pr; X = Cl, Br) have shown that loss of L is the initial reaction, and for both R_2S and R_2SO the activation energies (and first-order rate constants) decrease in the order Me > Et > Pr (*333*). Detailed studies of both the thermal and photochemical cis/trans isomerism of simple $[Pt(S\text{-}R_2SO)_2Cl_2]$ complexes have also been reported (*74*).

H. OTHER TECHNIQUES

ESR spectra of Fe(III), Co(II), and Cu(II) chlorides in Me_2SO solution have been reported (*197*). The spectrum of $FeCl_3$ in Me_2SO is of particular interest, as evidence suggests the presence of $[FeCl_4]^-$ ions. This supports the structural data for the Me_2SO complex of Fe(III), which show the presence of $[FeCl_2(O\text{-}Me_2SO)_4][FeCl_4]$ (*vide supra*). The Mössbauer spectrum of this system has also been reported (*435*).

The ESR spectrum of $[Cu(O\text{-}Me_2SO)_2Cl_2]$ has been described, and the observed *g*-values suggest an ionically bound Cu(II) species (*458*). ESR has also been applied to solution kinetics in the reaction of $[Cr(CN)_5(NO)]^{3-}$ with alkyl halides in Me_2SO solution, and it was demonstrated that the cyanide ligands undergo solvolysis in five discrete steps forming $[Cr(CN)_{5-n}(Me_2SO)_n(NO)]^{(n-3)-}$ (*396*). Studies of $[ML_3][ClO_4]_2$ complexes [M = Cu(II), Co(II), Ni(II); L = bis(phenylsulfinyl)methane (PSM), 1,2-bis(phenylsulfinyl)ethane] by ESR showed that the Cu(II) complex of PSM was dimeric, while all others were monomeric (*326*). An NQR study of the complex of empirical formula $[Hg(Me_2SO)Cl_2]$ strongly suggests that the complex is not a monomeric three-coordinate species; the presence of widely spaced signals (^{35}Cl and ^{37}Cl) suggests inequivalent chloride ligands, and so a halide-bridged species was proposed (*88*). The structural interpretation of this complex is further discussed below.

III. Models for Metal–Sulfoxide Bonding

Two major bonding models have been proposed in the literature to explain ambidentate sulfoxide coordination. The first is a valence bond rationale whereby the structure of simple sulfoxides is considered as a resonance hybrid of three canonical forms (Fig. 1). In *O*-bonding, form 1 is assumed to be dominant, and in *S*-bonding, form 3 is assumed to be dominant. In reality, the situation is more complicated, as form 2, which is the usual way to formalize an R_2SO unit, is not a true representation of the molecule. X-Ray spectroscopy (Section II,E) has shown that the free sulfoxide molecule is polarized and that form 1 is a better representation of the molecule. Indeed, considering the molecule in this form, one would expect aromatic groups attached to sulfur to decrease the positive charge via delocalization, whereas aliphatic groups would have little effect, regardless of chain length. These observations are borne out by experiment. As the canonical form 1 appears to be a good representation of the free sulfoxide, the molecule would be expected to coordinate to Lewis acids via the negative end of the dipolar unit. Coordination via oxygen would therefore be expected to be the

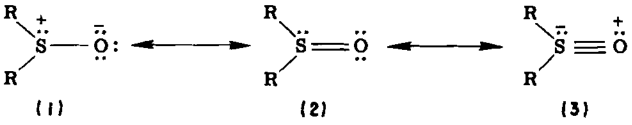


FIG. 1. Canonical forms contributing to the resonance hybrid of simple sulfoxides, R_2SO.

norm and indeed is observed in the vast majority of complexes. Transfer of electron density from oxygen to the metal center would have little effect on the positive charge carried by sulfur, and this is also confirmed by X-ray spectroscopy. In electron-counting terms, the oxygen atom may be envisaged as sp^2-hybridized; overlap with an sp^3-hybridized sulfur atom thus produces a single S—O σ-bond, leaving two long-pairs (sp^2) on oxygen for donation to a Lewis acid. The experimentally observed M—$\widehat{\mathrm{O}}$—S of 120° would thus be expected. The vacant low-lying d-orbitals of sulfur are available for overlap with the filled p-orbital of oxygen, and in consequence the extent of $d_\pi - p_\pi$ overlap would be expected to depend heavily on the environment of the oxygen atom. Thus, donation to a weak Lewis acid would have little effect on the extent of $d_\pi - p_\pi$ bonding, whereas donation to a strong Lewis acid would considerably decrease it. Experimental observations confirm that the S—O bond order is little affected by coordination via oxygen, and the more refined data (Section II,A) do suggest some decrease. This model suggests that the geometry about the sulfur atom will remain approximately tetrahedral and that the C—S bond lengths will be little affected by *O*-bonding, as observed. As *O*-bonding appears to involve donation from an sp^2-orbital, the effect on the electron density in the S—C σ-bond will be small, but would be expected to cause a slight deshielding of the α-protons in the ^{1}H-NMR spectra of such complexes. Coupling between the metal center and the α-protons $[^4J(\mathrm{M}{-}^1\mathrm{H})]$ would not be expected on this basis. Both these observations are experimentally confirmed by ^{1}H-NMR studies (Section II,C).

As the free sulfoxide unit is polarized with oxygen carrying a negative charge, it is initially hard to envisage why coordination to a Lewis acid via sulfur should ever occur. Some workers have suggested that the canonical form 3 is dominant in *S*-bonding (*229*), but the physical data for these complexes are not consistent with this. The positive charge on the sulfur atom is known to increase upon *S*-bonding (relative to the free molecule). In electron-counting terms, donation from the polarized form 3 will leave the sulfur atom effectively neutral, and this does not represent an increase in the positive charge. Alternatively, donation from form 2 will leave the sulfur atom with a formal positive charge which represents a decrease in the electron density on the sulfur atom (known to be $\sim$5.3 valence electrons in the free molecule). It seems likely on this basis that the canonical form 3 makes little contribution to the resonance hybrid in *S*-bonding. Structural data support this; thus the increase in the S—O bond order is more compatible with S=O than with S≡O. Tetrahedral coordination about sulfur (suggesting sp^3-hybridization) would be envisaged, and overlap with an sp-hybridized oxygen atom leaves two occupied p-orbitals on oxygen available for $d_\pi - p_\pi$ overlap with the low-lying d-orbitals of sulfur. The double-bond character of S—O would thus be dependent upon the environment of the sulfur atom. On this basis, sulfoxides would be expected to act as poor π-acceptors, as any electron deficiency at sulfur can readily be rectified by $d_\pi - p_\pi$ bonding (effectively, transfer of electron density from oxygen to sulfur). As coordination via sulfur appears to involve donation via an sp^3-hybridized sulfur atom, the effect on the C—S σ-bond would be considerable, and the resulting deshielding of the α-protons in the ^1H NMR of such a complex would be expected. On this basis, coupling between the metal center and the α-protons [$^3J(M-H)$] would appear likely and is indeed observed.

This simple valence-bond rationale, involving a resonance hybrid of forms 1 and 2, appears to explain many of the physical data available for sulfoxide complexes. It appears that *S*-bonding does not involve such a major internal rearrangement of the molecule as one may initially expect and is almost certainly a result of the increased orbital diffuseness on passing from oxygen to sulfur. Thus with typical hard acids (see ref. *437*), orbital overlap will be most favorable with the less diffuse donor orbital of oxygen. In the case of typical soft metals, this overlap is less favorable due to the orbital diffuseness of the soft acid, and so coordination via sulfur occurs, where the orbital diffuseness of the donor and acceptor are more evenly matched.

Cases where sulfoxides coordinate to soft metals via oxygen are now known, and these require some comment. The first reports of such a complex concerned the $[Pd(Me_2SO)_4]^{2+}$ cation (*475, 476*), shown to be *cis*-$[Pd(O\text{-}Me_2SO)_2(S\text{-}Me_2SO)_2]^{2+}$ by a variety of techniques. Since that time, many other similar complexes have been reported, including $[Pd(O\text{-diisoamylsulfoxide})_4]^{2+}$ (*447–449*), $[Ru(O\text{-}Me_2SO)(S\text{-}Me_2SO)_3Cl_2]$ (*400*), $[Pd(Ph_2PCH_2CH_2PPh_2)(O\text{-}Me_2SO)_2]^{2+}$ (*143*), and several others (*142*). This rather unusual phenomenon has been rationalized by both electronic and steric considerations. It has been proposed (*437*) that this is an example of "anti-symbiosis," whereby the metal center retains its degree of electroneutrality by coordination of sulfoxide moieties via the diffuse (sulfur) and nondiffuse (oxygen) donors. While this may well be part of the explanation for this phenomenon, steric constraints appear to be another factor. Thus, in the complex $[Pd(Ph_2PCH_2CH_2PPh_2)(O\text{-}Me_2SO)_2]^{2+}$, the large diphosphine ligand, with a cone angle of 125° (*488*), makes coordination via sulfur extremely sterically hindered. Use of molecular models has shown coordination via oxygen to be less sterically demanding (*143*). Similar arguments can be applied to the $[Pd(O\text{-diisoamylsulfoxide})_4]^{2+}$ cation, the first totally *O*-bonded homoleptic sulfoxide complex of a soft metal.

Although the simple valence-bond rationale of ambidentate sulfoxide coordination appears adequate for most purposes, attempts have been made to produce a more sophisticated model by utilization of the structural and X-ray spectroscopic data of Me_2SO as the basis for a semiempirical calculation of its electronic structure (*48*). The results of these calculations suggest that the S—O bond consists of one filled σ-bonding orbital and a pair of d_π-orbitals containing electron density equivalent to about half an electron in total. This charge density is said to originate from the oxygen p-orbitals. Additionally, these calculations imply that there are lone-pairs on both sulfur (largely sp-type) and oxygen (largely s-type). On this basis, it is assumed that the S—O bond order is about $1^1/_4$. Utilizing the results of the semiempirical calculations, the relative energies of the orbitals may be placed in a series; thus the p_π-orbitals largely associated with oxygen are calculated to have energies of -9.5 and -10.1 eV, the σ-electron-pair of sulfur an energy of -14.92 eV, and the σ-electron-pair of oxygen an energy of -23.9 eV. From the relative orbital energies, it has been proposed that oxygen bonding is the result of donation from the p_π-orbital largely associated with oxygen, and that sulfur bonding is the result of donation from the σ-electron-pair of sulfur. If this is indeed the case, then the observation of *O*-bonding necessitates having an acceptor with an incomplete t_{2g} orbital to accommodate the p_π-electron density. It has been claimed (*48*) that in cobalt(III) sulfoxide complexes the Co(III) ion has the configuration $(t_{2g})^4(e_g)^2$ and can thus form *O*-R_2SO complexes. This is compared with rhodium(III), which has the configuration $(t_{2g})^6$ and thus is incapable of forming *O*-R_2SO complexes. In reality, it seems doubtful that Co(III) is high spin in these complexes, as this paramagnetic ground state occurs only with very weak-field ligands (such as F^- in $[CoF_6]^{3-}$ and $[Co(H_2O)_3F_3]$). Electronic spectral data also suggest that the easily polarized R_2SO moiety causes a large degree of splitting in highly charged complexes (Section II,D). A Co(III) sulfoxide complex has been proposed (*410*), formulated as $[Co(O\text{-}Me_2SO)_4I_2][I]$, with an effective magnetic moment of 4.45 μ_B. The method of preparation (from cobaltous iodide, iodine, and dimethyl sulfoxide) suggests the possibility that the product may contain Co(II). It should be noted that observed moments for Co(III) are ~5.4 μ_B, while those for Co(II) are 4.1–5.2 μ_B (*131*). Reported moments for Co(II) sulfoxide complexes include $[Co(O\text{-}Me_2SO)_2\{N(CN)_2\}_2]$, 4.90 μ_B (*329*), and $[Co(O\text{-}Me_2SO)(CH_2ClCOO)_2]$, 4.96 μ_B (*107*). Accordingly, it seems likely that Co(III) sulfoxide complexes are low spin and as such have the diamagnetic ground state $(t_{2g})^6$. In addition, this model does not seem satisfactory in explaining *O*-bonding in certain complexes of soft metals (*vide supra*). As such, the simple valence-bond rationale mentioned previously is the preferred model.

IV. The Chemistry of Sulfoxide Complexes

A. THE CIS AND TRANS EFFECT AND INFLUENCE IN SULFOXIDE COMPLEXES

The trans effect can effectively be defined as "the effect of a coordinated group on the rate of the substitution reactions of ligands opposite to it in a metal complex" (*50*). The importance of this effect in both preparative coordination chemistry and kinetics, particularly of square-planar complexes, should not be underestimated. The trans influence of a ligand is a ground-state effect and refers to the ability of a ligand to weaken (lengthen) a bond trans to itself. The cis effect and influence of ligands have frequently been disregarded, as the effects are usually minor in comparison with the trans effect and influence. However, especially when groups of approximately equal trans effect are present in a complex, the cis effect can dominate the kinetics of reaction (*267*). Work on determining the magnitude of these effects in sulfoxide complexes has been almost solely due to Kukushkin and his co-workers, and reviews on this specific subject have appeared (Table I). Accordingly, results of this research will only be summarized, with discussion, here.

1. *Infrared Spectroscopic Studies*

To account for a ligand's trans effect, theories based on both σ-donor power (*239*) and π-bonding ability (*112*) have been proposed. Kukushkin's group has investigated the σ-donor power/π-bonding ability of sulfoxides by using infrared spectroscopy and produced several "trans effect series." In reality, the measurements reflect the trans influence of a ligand, rather than its trans effect. The complexes [M][Pt(*S*-Me_2SO)Cl_3] (M = K, Cs, Et_3NH) exhibit a band at 310 cm^{-1} assigned as ν(M—Cl) trans to the *S*-Me_2SO ligand (*288*). This is compared with other reported values of ν(M—Cl) for various trans groups (*157*), and these authors conclude that the similar values of ν(M—Cl) for *trans*-*S*-Me_2SO and *trans*-ethylene indicate similar degrees of π-bonding. The use of infrared data in this manner requires detailed knowledge of the force constants involved, relatively few of which have even been evaluated, because of interactions between various infrared-active modes in the complex. This point has been elaborated upon previously (see Section II,B). Other essentially similar "trans effect series" have been produced (*214, 348*) which are subject to similar constraints. The values of ν(CO) and ν(Pd—C) in the complexes *trans*-[Pd(S-R_2SO)(CO)Cl_2] (R = Me, Et, benzyl) have been correlated with the variations in π-acceptor abilities of the sulfoxide ligands (*22*). Additionally, it was observed that ν(S=O) is at a lower frequency in *trans*-[Pd(S-R_2SO)(CO)Cl_2] than in [Pd(S-R_2SO)Cl_2]$_2$, and this is explained in terms of reduced π-back-donation from the metal center to the $p_\pi - d_\pi$ orbital of the S—O bond in the former complex because of competition for metal π-electron density from the *trans*-carbonyl group. It was previously pointed out that the value of ν(S=O) is dependent on various factors (see Section II,B), and undoubtedly crystallographic data give the best indication of the extent of metal–ligand π-bonding. Consideration of such data suggests that sulfoxides are modest π-acceptors, with an overall trans influence (due to both σ- and π-effects) similar to ethylene (Table VI).

2. *The Analogy between Sulfoxides and Olefins*

Crystallographic studies have suggested that sulfoxides have a trans influence similar in magnitude to, although slightly less than, that of ethylene (Table VI). Kukushkin's group has produced several results which also suggest that the trans influences of these ligands are similar in magnitude. Thus, the stability constants of reaction (4) are reported to be similar in magnitude for both L = S-Me_2SO and L = ethylene (*351*).

$$[PtLCl_3]^- \underset{}{\overset{K_1}{\rightleftharpoons}} [PtL(H_2O)Cl_2] \overset{K_2}{\rightleftharpoons} [PtL(H_2O)_2Cl]^+ \overset{K_3}{\rightleftharpoons} [PtL(H_2O)_3]^{2+} \qquad (4)$$

The kinetics and mechanism of ligand substitution reactions of square-planar platinum(II) dimethyl sulfoxide complexes have been exhaustively studied (*173*), and these workers conclude that the cis and trans influences and the trans effects of Me_2SO and ethylene are similar in magnitude whereas the cis effect of Me_2SO is about 100 times as large as that of ethylene. The results for reaction (5), where the stability constants, K_1, are reported to be 1.5×10^8 (L = S-Me_2SO) and 4.5×10^8 (L = ethylene) corroborate this analogy (*213*).

$$[Pt(NH_3)_3L]^+ + H_2O \overset{K_1}{\rightleftharpoons} trans\text{-}[Pt(NH_3)_2(H_2O)L] \qquad (5)$$

Results from preparative studies support both S-Me_2SO and ethylene having high trans effects. Thus, the products of both reactions (6) and

(7) are of cis configuration,

$$[\mathrm{K}][\mathrm{Pt}(S\text{-}\mathrm{Me_2SO})\mathrm{Cl_3}] + \text{ethylene} \rightarrow cis\text{-}[\mathrm{Pt}(S\text{-}\mathrm{Me_2SO})(\text{ethylene})\mathrm{Cl_2}] \qquad (6)$$

$$[\mathrm{K}][\mathrm{Pt}(\text{ethylene})\mathrm{Cl_3}] + \mathrm{Me_2SO} \rightarrow cis\text{-}[\mathrm{Pt}(S\text{-}\mathrm{Me_2SO})(\text{ethylene})\mathrm{Cl_2}] \qquad (7)$$

implying that an olefin–Pt–S-Me_2SO axis is unstable (*345*). Attempts to prepare sulfoxide complexes of higher olefins (*346*) and allyl derivatives (*289*) support these results.

Isotopic exchange studies on $[Pt(ethylene)Cl_3]^-$ (*240*) and $[Pt(S\text{-}Me_2SO)Cl_3]^-$ (*355*) have shown that the chloride ligands trans to both ethylene and S-Me_2SO are exchanged "instantaneously," again supporting the analogy.

3. *Thermal Analysis Studies*

Although sulfoxides exhibit a relatively high trans effect, thermal analysis studies have shown that it is the cis-substituted product, and not the trans-substituted product, which has the lower free energy (*340*). Thus, DTA of *trans*-$[Pt(S\text{-}Me_2SO)(NH_3)Cl_2]$ shows endothermic (due to melting) and exothermic (due to isomerization) effects, without weight loss, whereas *cis*-$[Pt(S\text{-}Me_2SO)(NH_3)Cl_2]$ shows neither endothermic nor exothermic effects without a loss in weight. Certain results from thermal analysis cannot be explained by the high trans effect of the S-R_2SO moiety; thus, on heating $[Pt(NH_3)_3L][X]_2$ (L = Me_2S, S-Me_2SO; X = Cl, Br), the initial reaction is loss of L, not loss of ammonia (*23*). The explanation of this result requires a consideration of both the trans effect of each ligand and the M–ligand bond strength. The weak M–S-Me_2SO bond is cleaved despite the high trans effect of the sulfoxide moiety.

The different steric requirements of nPr$_2$SO and iPr$_2$SO lead to the isolation of *trans*- and *cis*-$[PtL_2Cl_2]$ species, respectively, from the interaction of the $[PtCl_4]^{2-}$ ion with the appropriate sulfoxide. Thermal analysis of *trans*-$[Pt(S\text{-}n\mathrm{Pr}_2SO)_2Cl_2]$ shows ready isomerization to the cis form, whereas *cis*-$[Pt(S\text{-}i\mathrm{Pr}_2SO)_2Cl_2]$ is stable, demonstrating that the R_2SO moiety will kinetically labilize chloride ligands in both cis and trans positions (*350*). It is also noteworthy that the complexes *trans*-$[Pt(S\text{-}Me_2SO)(Am)X_2]$ are thermally isomerized to the cis form (Am = ethanolamine, X = Cl, Br), but *cis*-$[Pt(S\text{-}Me_2SO(Am)I_2]$ is thermally isomerized to the trans form. This is undoubtedly a result of the decrease in trans effect, $I^- >>> Br^- \sim Cl^-$ (*343*).

4. *Studies on Sulfoxide–Amine Complexes*

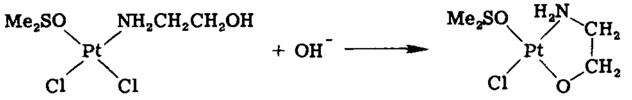
Consideration of the reactions of Eqs. (8) and (9) for a variety of systems [e.g., R = Me, X = Cl, Am = NH_3, pyridine (*356*); R = Me,

$X = Br$, $Am = NH_3$, pyridine, CH_3NH_2, etc. (*353*); $R_2SO = (CH_2)_4SO$, $X = Cl$, $Am = NH_3$, pyridine (*344*)] has been cited as a demonstration of the high trans effect of the S-R_2SO moiety.

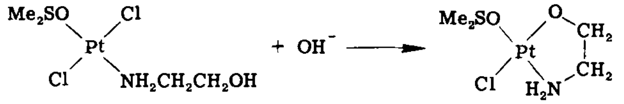
$$[K][Pt(S\text{-}R_2SO)X_3] + Am \rightarrow \mathit{trans}\text{-}[Pt(S\text{-}R_2SO)(Am)Cl_2] \qquad (8)$$

$$[K][Pt(Am)X_3] + R_2SO \rightarrow \mathit{cis}\text{-}[Pt(S\text{-}R_2SO)(Am)Cl_2] \qquad (9)$$

A comparison of the cis and trans effects of S-Me_2SO has been made by consideration of the rates of the reactions in Eqs. (10) and (11). Ring closure via halide labilization trans to S-Me_2SO is more rapid than closure via labilization cis to S-Me_2SO, indicating that the trans effect of the S-Me_2SO moiety exceeds its cis effect (*361*).



(10)



(11)

5. *Carbonylation Reactions*

Palladium(II) halide-bridged dimeric complexes of the type $[Pd_2L_2Cl_4]^{n-}$($L = S$-R_2SO, R_2S, Cl, CO, NH_3) are cleaved by carbon monoxide to yield monomeric *trans*-$[Pd(L)(CO)Cl_2]$ species. The rates of some cleavage reactions have been measured (*20*) and found to vary with L, such that $Et_2S > S$-$Me_2SO >> Cl^- > CO \sim NH_3$. The high trans effect of S-Me_2SO causes rapid cleavage of the trans-halide bridge. Variation in rate constant for this reaction with the nature of the sulfur donor has been measured (*21*), and a trans effect series constructed: $Et_2S > S$-$Me_2SO > S$-$Et_2SO > (CH_2)_4S$.

B. GENERAL PREPARATIVE TECHNIQUES

Several methods have been widely used in the preparation of sulfoxide complexes, and these are outlined below. Routes specific to given systems are dealt with in Section V.

1. *Direct Metal–Ligand Reactions*

For the preparation of simple $[M(O\text{-}R_2SO)_n][X]_m$ salts (X = uncoordinated anion; n, m = integer), the mixing of a hydrated metal salt with the appropriate sulfoxide is often sufficient. An appropriate solvent must be chosen, if this is considered necessary, as the solvent may affect the course of the reaction. Thus, acetone was successfully used as solvent in the preparation of a range of complexes of the type $[M(O\text{-}Me_2SO)_6][ClO_4]_2$ (M = Mn, Co, Fe) (*95*), largely as a route to anhydrous salts, but attempts to prepare $[M(O\text{-}\{C_6H_5CH_2\}_2SO)_6][ClO_4]_2$ using acetone as solvent led only to the isolation of $[M(O\text{-}\{C_6H_5CH_2\}_2SO)_4(Me_2CO)_2][ClO_4]_2$ (M = Mn, Fe, Co, Ni, Zn, Cu). Using *t*-butanol as solvent gave the desired products (*497*).

Care must also be taken to obtain the correct reaction conditions; deoxygenation reactions of sulfoxides have been known to occur during relatively simple preparative procedures (see Section IV,C). In addition, displacement of other ligands can easily occur, as, for example, in Eqs. (12) and (13).

$$[Ru(EPh_3)_2(MeOH)X_3] + 1{:}1\ H_2O/Me_2SO \xrightarrow{\text{shake 24 hours}} [Ru(EPh_3)_2(Me_2SO)X_3] \quad (12)$$

$$[Ru(EPh_3)_2(MeOH)X_3] + Me_2SO \xrightarrow{\text{shake 24 hours}} [Ru(Me_2SO)_4Br_2] \quad (E = P,As) \quad (13)$$

The relatively minor alteration in reaction conditions can be seen to drastically alter the nature of the product (*468*). In addition many sulfoxide complexes are thermally degraded, and in consequence the extent of drying can alter the nature of the product. Thus, the complex $[Co(O\text{-}Me_2SO)_6][I]_2$ is isolated from a cobaltous iodide–dimethyl sulfoxide system, but extensive drying *in vacuo* causes degradation to yield $[Co(O\text{-}Me_2SO)_6][CoI_4]$ (*128*).

2. *Use of Dehydrating Agents*

Dehydrating agents have commonly been employed in the preparation of lanthanide sulfoxide complexes from hydrated lanthanide salts. For example, dimethoxypropane has been used to prepare both $(CH_2)_4SO$ (*65*) and $n\text{Pr}_2SO$ (*56*) complexes of the lanthanide nitrates. An alternative dehydrating agent is ethyl orthoformate [Eq. (14)].

$$(C_2H_5O)_3CH + H_2O \rightarrow 2C_2H_5OH + C_2H_5OOCH \quad (14)$$

This powerful dehydrating agent was initially used in the preparation of nickel sulfoxide complexes (*244*), but has found wider application in the chemistry of lanthanide sulfoxide complexes (*189*).

3. *Halide Abstraction Reactions*

The technique of performing halide abstraction via interaction of a metal halo complex with a silver(I), thallium(I), or nitrosonium salt (see ref. *142*, for discussion) has proved useful in the isolation of many novel sulfoxide complexes. Thus, $[Pd(S\text{-}Me_2SO)_2(O\text{-}Me_2SO)_2]$-

$[ClO_4]_2$ was prepared in this manner from palladium(II) chloride (*475*), and similarly $[Pd(dien)(S\text{-}Me_2SO)][ClO_4]_2$ (*116*) and $[Pd(Ph_2PCH_2CH_2PPh_2)(O\text{-}Me_2SO)_2][ClO_4]_2$ (*143*) were prepared via halide abstraction [Eqs. (15) and (16)].

$$[Pd(dien)I][I] + 2AgClO_4 \xrightarrow{Me_2SO} [Pd(dien)(S\text{—}Me_2SO)][ClO_4]_2 \qquad (15)$$

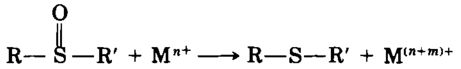
$$[Pd(Ph_2PCH_2CH_2PPh_2)Cl_2] + 2AgClO_4 \xrightarrow{Me_2SO} [Pd(Ph_2PCH_2CH_2PPh_2)(O\text{—}Me_2SO)_2][ClO_4]_2 \qquad (16)$$

C. DEOXYGENATION REACTIONS

Sulfoxides are very important intermediates in organic synthesis. To the organosulfur chemist, it is frequently desirable to transform a sulfoxide into the corresponding thioether. To the general organic chemist, the complete removal of a sulfoxide moiety may be necessary, and a two-step process is frequently used. Initially, the sulfoxide is reduced to the thioether, and then further reduction is performed with Raney nickel, lithium in liquid ammonia, or related reductants. It is therefore apparent that the transformation of R_2SO into R_2S is of more than academic interest and that metal-ion-induced deoxygenations (especially those that are catalytic) will be of great interest in organic chemistry. The subject of sulfoxide deoxygenation has been exhaustively reviewed (Table I), but with the emphasis on organic preparative studies. Here, deoxygenations resulting from interactions of sulfoxides with the early transition metals, which have found preparative applications, and with the platinum group metals, which have only really developed in the last decade, will be considered.

1. The Early Transition Metals

Titanium(III) chloride has been used both as a reagent for the quantitative determination of sulfoxides (*49, 247*) and preparatively in the reduction of sulfoxides, R_2SO ($R = n$Bu, Ph, benzyl) to the corresponding thioethers. The attraction of using low-valent early transition metals as reductants is the high selectivity of the reaction as shown in Eq. (17).



$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{S}\text{—}R' + M^{n+} \longrightarrow R\text{—}S\text{—}R' + M^{(n+m)+} \qquad (17)$$

Thus, the above-mentioned reductions occur in 68–91% yields (*276*). A slow reduction has also been observed using aqueous vanadium(II) chloride. The reaction requires rather severe conditions (~100°C at 40 torr for 8 hours to obtain 78–91% yields) (*277*). Sulfoxide deoxygenation also occurs with niobium and tantalum pentahalides of the type $[MX_5]$ (M = Nb, Ta; X = Cl, Br), yielding halogenated sulfides and coordinating further sulfoxide ligands to the resulting oxyhalide (*125*), as shown in Eq. (18).

$$[NbCl_5] + 3Me_2SO \rightarrow [NbOCl_3(O\text{—}Me_2SO)_2] + \begin{array}[t]{c} Me_2SCl_2 \\ \downarrow \\ ClCH_2SCH_3 + HCl \end{array} \tag{18}$$

No such deoxygenation is observed with the corresponding fluorides, whose reaction is more straightforward (*183*) [Eq. (19)].

$$[MF_5] + 2Me_2SO \rightarrow [MF_5(O\text{-}Me_2SO)_2] \qquad (M = Nb, Ta) \tag{19}$$

A similar deoxygenation occurs in the reaction between $[MoCl_5]$ and dimethyl sulfoxide (*464*), yielding the oxychloride complex $[MoOCl_3(Me_2SO)]$. The corresponding reaction with Ph_2SO yields only the complex $[MoCl_5 \cdot Ph_2SO]$ (*250*). A novel deoxygenation has been noticed as an extension of the epoxide reduction system based on cocondensation of metal atoms (M = Ti, V, Cr, Co, Ni) with the epoxide, whereby atomic chromium will deoxygenate Me_2SO via formation of a red matrix (*210*). The system awaits development. An effective reducing system has been developed (*277*) by the activation of molybdenum oxychloride using zinc dust. Sulfoxide reduction was accomplished at room temperature in 1 hour with high yields. A molybdenum(IV) derivative has also been reported as a deoxygenation reagent (*403*) [Eq. (20)].

$$[MoO(S_2CNEt_2)_2] + Me_2SO \rightarrow [MoO_2(S_2CNEt_2)_2] + Me_2S \tag{20}$$

Color changes from pink via purple to yellow were observed. A variety of molybdenum(II) and -(III) and tungsten(III) complexes are also active reductants. Complexes including $[NH_4][MoCl_8] \cdot NH_4Cl$, $[Cs]_3[Mo_2Cl_8H]$, $[K]_3[MoCl_6]$, and $[K]_3[W_2Cl_9]$ have been reported (*418*) as highly active (70–99% yields) under very mild conditions. Iron pentacarbonyl has also shown some promise as a sulfoxide reductant, although rather high temperatures (~130°C) are required (*12*).

2. *The Platinum Group Metals*

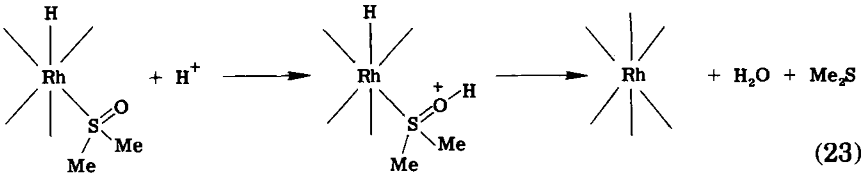
Ruthenium halides in Me_2SO solution under an atmosphere of hydrogen are known to form complexes of the type $[RuX_2(Me_2SO)_4]$

(X = Cl, Br), and reduction of the solvent has been observed in the case of the bromide complex [Eq. (21)] (*304*).

$$\mathrm{Me_2SO} \xrightarrow{\mathrm{RuBr_3/H_2}} \mathrm{Me_2S + H_2O} \tag{21}$$

Solutions of [$RhCl_3 \cdot 3H_2O$] in Me_2SO will perform this reduction catalytically. The proposed mechanism (*303*) involves insertion of Me_2SO into a Rh—H bond, as shown in Eqs. (22) and (23).

$$[\mathrm{RhCl_3(Me_2SO)_3}] + \mathrm{H_2} \rightarrow [\mathrm{RhCl_2(H)(Me_2SO)_2}] + \mathrm{HCl} \tag{22}$$



(23)

The generated thioether may be either free or coordinated, depending upon the stability of the resulting complex, as [$RhCl_3(Et_2S)_3$] is also a catalyst for this reduction. This suggests that the observed decrease in catalytic activity with time is not due to the formation of an inactive thioether complex. Indeed, as the system can be made autocatalytic using H_2/O_2 mixtures, the decrease in activity caused by the use of pure hydrogen is probably a result of dissociation of the hydrido species, as shown in Eq. (24).

$$[\mathrm{Rh(III)—H}]^{n+} \rightarrow [\mathrm{Rh(I)}]^{(n-1)+} + \mathrm{H^+} \tag{24}$$

Similar mechanistic arguments can be applied to the ruthenium system mentioned above.

The use of sulfoxide complexes as homogeneous hydrogenation catalysts is now being investigated (*vide infra*), and during these investigations it was observed that attempts to generate hydrido species by oxidative addition of hydrogen or hydrogen chloride to Rh(I) sulfoxide complexes normally results in sulfoxide reduction, which may be accompanied by metal formation. Even in the presence of olefin, these reductions occur in preference to olefin hydrogenation (*302*). Sulfoxide deoxygenation reactions have also been observed during preparative procedures with palladium(II) and platinum(II). The products of such reactions are frequently dependent upon reaction conditions; for example, palladium(II) chloride reacts with $(CH_2)_4SO$ at low temperature to yield the bis(*S*-sulfoxide) complex [Eq. (25)].

$$[PdCl_2] + 2(CH_2)_4SO \xrightarrow{\text{cool}} [Pd(\mathit{S}\text{—}\{CH_2\}_4SO)_2Cl_2] \qquad (25)$$

In the presence of acetone and hydrochloric acid at higher temperatures deoxygenation results (*164*) [Eq. (26)].

$$[PdCl_2] + 2(CH_2)_4SO \xrightarrow{\text{acetone/HCl/warm}} [Pd(S\{CH_2\}_4)Cl_2] \qquad (26)$$

Problems of dilution and pH sensitivity have also been encountered in the synthesis of *cis*-[Pt(*S*-R_2SO)(olefin)Cl_2] complexes (*85*), where deoxygenation of the sulfoxide with concomitant oxidation of the metal center occurs at low pH. The reactions of [M($Ph_2PCH_2CH_2PPh_2$)Cl_2] (M = Pd, Pt) with one equivalent of silver(I) perchlorate in the presence of Me_2SO yield either the *O*-Me_2SO complex or its deoxygenation product, depending upon reaction conditions. A sequence of reactions, Eq. (27), has been proposed (*143*).

$$\begin{tikzcd}
{[M(Ph_2PCH_2CH_2PPh_2)Cl_2] + AgClO_4} \arrow[r, "Me_2SO"] & {[M(Ph_2PCH_2CH_2PPh_2)(\mathit{O}\text{-}Me_2SO)Cl][ClO_4]} \arrow[d] & (27) \\
{\tfrac{1}{2}[M_2(Ph_2PCH_2CH_2PPh_2)_2Cl_2][ClO_4]_2} & {[M(Ph_2PCH_2CH_2PPh_2)(Me_2S)Cl][ClO_4]} \arrow[l] &
\end{tikzcd}$$

The complex anion $[Pt(\mathit{S}\text{-}Me_2SO)Cl_3]^-$ undergoes an internal redox reaction in acidic media, and evidence for the formation of Pt(IV) species and Me_2S has been presented (*466*). This may be an explanation for the deoxygenation of $(CH_2)_4SO$ previously mentioned (*164*). The oxidation of Pt(II) to Pt(IV) with concomitant reduction of Me_2SO to Me_2S has been accomplished using hydrochloric acid (*357*), as shown in Eq. (28).

$$[Pt(\mathit{S}\text{-}Me_2SO)_2Cl_2] + 4HCl \rightarrow [Pt(Me_2S)_2Cl_4] + Cl_2 + 2H_2O \qquad (28)$$

In the presence of added tin chloride, the reaction is reported to be more synthetically useful (*27*). Using this technique, Pt(IV) thioether complexes may be synthesized directly from the salts of the $[PtCl_4]^{2-}$ ion, Eq. (29) (*29*).

$$[K]_2[PtCl_4] + SnCl_2 + HCl + Me_2SO \rightarrow \mathit{trans}\text{-}[Pt(Me_2S)_2Cl_4] \qquad (29)$$

A trace of the cis-isomer is also produced.

It is noteworthy that under certain reaction conditions, the complex $[Pt\{Sn(\mathit{O}\text{-}Me_2SO)Cl_2\}_5][Cl]_2$ has been reported as a product of this reaction (*28*).

3. *Other Deoxygenations*

Silver(I)-ion-assisted Me_2SO oxidations of organic halides have been observed for primary and secondary bromides and iodides (*174*). The reactions occur under ambient conditions yielding the corresponding carbonyl, plus traces of alcohol. The fate of the silver(I) ion is unreported.

D. OXYGENATION REACTIONS

Metal-ion-induced oxygenations of the types $R_2S \rightarrow R_2SO$ and $R_2SO \rightarrow R_2SO_2$ are known to occur, either stoichiometrically or catalytically, and these are considered below.

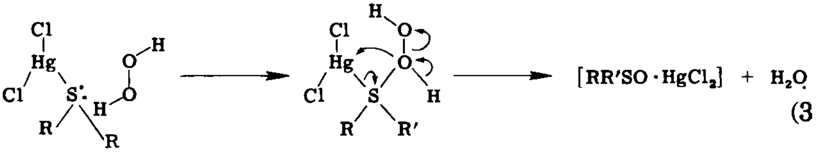
1. *Thioether Oxygenations*

The complex $[RuBr_3(NO)(Et_2S)_2]$ reacts with dissolved oxygen in chloroform solution containing a source of protons (such as ethanol) under irradiation with light of wavelength 380–480 nm to yield the *O*-Et_2SO complex, $[RuBr_3(NO)(O\text{-}Et_2SO)]_2$. This complex was the subject of X-ray crystallographic analysis (Table VIII, *191*). Oxidation of coordinated Me_2S to Me_2SO has been observed by ^{1}H-NMR spectrometry after recrystallization of the complex *trans*-$[Pt(Me_2S)_2Br_2]$ from hot water. *cis*-$[Pt(Me_2S)(S\text{-}Me_2SO)Br_2]$ was identified as an impurity in the product (*225*).

Mercury chloride thioether complexes have been oxidized to the corresponding sulfoxide complexes by treatment with hydrogen peroxide (*76*) [Eq. (30)]

$$[RR'S{\cdot}(HgCl_2)_n] \xrightarrow{H_2O_2} [RR'SO{\cdot}(HgCl_2)_m] \qquad (30)$$

where R = R′ = Me, Et, *n*Pr, *i*Pr, *n*Bu, *i*Bu, Ph; R = Me, R′ = Et; $n = 1$ or 2; $m = 1, 1.5,$ or 2. A mechanism is proposed which is consistent with infrared data suggesting an *O*-bonded product [Eq. (31)].



(31)

Other workers have formulated mercury sulfoxide complexes as *S*-bonded, and this is discussed in Section VI; in addition, NQR data (see Section I,H) suggest that these complexes are in fact dimeric in nature.

2. *Sulfoxide Oxygenations*

Kinetic studies of the redox reaction observed between Cr(VI) and Me_2SO gave no evidence of complex formation (*408*). The overall reaction, Eq. (32), shows Me_2SO is oxidized to the sulfone.

$$2[HCrO_4]^- + 3Me_2SO \rightarrow 2Cr(III) + 3(Me_2SO_2) \qquad (32)$$

A Cr(VI) sulfoxide complex has been postulated after interaction of $[CrO_2Cl_2]$ with Me_2SO (*385*), but the complex was uncharacterized as it was excessively unstable. It was observed that hydrolysis of the product led to the formation of dimethyl sulfone. The action of hydrogen peroxide on mesityl ferrocencyl sulfide in basic media yields both mesityl ferrocenyl sulfoxide (21%) and the corresponding sulfone (62%) via a reaction similar to the Smiles rearrangement (*165*). Catalytic air oxidation of sulfoxides by rhodium and iridium complexes has been observed. Rhodium(III) and iridium(III) chlorides are catalyst percursors for this reaction, but ruthenium(III), osmium(III), and palladium(II) chlorides are not (*273*). The metal complex and sulfoxide are dissolved in hot propan-2-ol/water (9:1) and the solution purged with air to achieve oxidation. The metal is recovered as a noncrystalline, but still catalytically active, material after reaction (*272*). The most active precursor was $[IrHCl_2(S\text{-}Me_2SO)_3]$, and it was observed that alkyl sulfoxides oxidize more readily than aryl sulfoxides, while thioethers are not oxidized as complex formation occurs.

E. CATALYSIS BY SULFOXIDE COMPLEXES

In addition to the catalysis of sulfoxide deoxygenation (Section IV,C) and sulfoxide oxygenation (Section IV,D), other interesting reactions have been shown to be catalyzed by sulfoxide complexes, and these are detailed below.

1. *Catalytic Decomposition of Hydrogen Peroxide*

Palladium(II) sulfoxide complexes are active catalyst percursors for the decomposition of hydrogen peroxide. Complexes of the types $[Pd(S\text{-}Me_2SO)_2X_2]$, $[Pd(S\text{-}Me_2SO)X_2]_2$, and $[K][Pd(S\text{-}Me_2SO)Cl_3]$ have been examined (*358*), and all are more active than the corresponding $[PdX_4]^{2-}$ (X = Cl, Br) species. The activity increases with catalyst precursor concentration until a plateau of activity is reached. At low concentrations, the bromide complexes are more active than the chloride complexes, but at the plateau region, the order is reversed. Additionally, the bridged species are found to be less active than the corresponding monomeric complexes. A detailed mechanism has been proposed (*352*) which suggests a palladium peroxo species may be the active catalyst.

2. *Oligomerization and Polymerization Reactions*

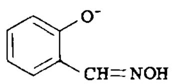
The patent literature contains several references to the use of sulfoxide complexes, usually generated *in situ,* as catalyst precursors in oligomerization and polymerization reactions. Thus, a system based upon bis(acrylonitrile)nickel(0) with added Me_2SO or Et_2SO is an effective cyclotrimerization catalyst for the conversion of butadiene to cyclo-1,5,-9-dodecatriene (*44*). A similar system based on titanium has also been reported (*407*). Nickel(II) sulfoxide complexes, again generated *in situ,* have been patented as catalyst precursors for the dimerization of propene (*151*) and the higher olefins (*152*) in the presence of added alkyl aluminum compounds.

The use of palladium(II) sulfoxide complexes as catalyst precursors for polymerization has met with mixed results; thus a report of a palladium(II) chloride–dimethyl sulfoxide system as a catalyst precursor for phenylacetylene polymerization suggests similar results to those obtained using tin chloride as catalyst precursor (*421*). However, addition of dimethyl sulfoxide to solutions of $[NH_4]_2[PdCl_4]$ decreases the activity as a catalyst precursor for the polymerization of butadiene (*100*). Dimethyl sulfoxide complexes of iron have also been mentioned as catalyst precursors for styrene polymerization (*141*).

3. *Hydroformylation Reactions*

Although sulfoxide complexes have been studied as hydrogenation catalysts (*vide infra*), little work on the related hydroformylation reaction has been reported. A patent by B.P. (*196*) covers the use of

$[Rh(S\text{-}Me_2SO)(CO)(Sal)]$ (Sal =



)

as a catalyst precursor. The complex catalyzed the 100% conversion of a 500-fold excess of olefin (hexene, heptene, octene) to normal aldehydes (36%), branched aldehydes (59%), and alkanes (5%) at ~80°C with pressures of H_2/CO (1:1) of 350–1000 psig over 10 hours.

4. *Hydrogenation Reactions*

Sulfur donors are well known as poisons for heterogeneous catalysts, and a consequence of this is that possible homogeneous systems, incorporating sulfur donors, have been little studied. In the last decade, work on platinum metal complexes of sulfur donors, including sulfoxides, has shown the analogy between heterogeneous and homogeneous systems to be largely unfounded.

a. Hydrogen-Transfer Reactions. The catalytic system for air oxidation of sulfoxides to sulfones developed by Trocha-Grimshaw and Henbest (Section IV,D) has also found application as a catalyst for hydrogen transfer to unsaturated organic substrates. A series of iridium sulfoxide complexes, obtainable from chloroiridic acid, Eq. (33), have been examined (*259*).

$$\begin{tikzcd} \underset{(1)}{H_2IrCl_6} \arrow[r] & \underset{(2)}{cis\text{- and } trans\text{-}H[IrCl_4(S\text{—}Me_2SO)_2]} \arrow[r] & \underset{(3)}{[IrCl_3(S\text{—}Me_2SO)_2(O\text{—}Me_2SO)]} \arrow[d] \\ & & \underset{(4)}{[IrHCl_2(S\text{—}Me_2SO)_3]} \end{tikzcd} \tag{33}$$

Thus, the hydrido complex **4**, obtained by refluxing complexes **2** in propan-2-ol for 4 hours (*271*), catalyzes the conversion of 4-*tert*-butylcyclohexanones to axial (77%) and equatorial (23%) alcohols. The mechanism of hydrogen transfer from propan-2-ol to the substrate appears to be complex; traces of water in the system assist hydrogen transfer, as in anhydrous conditions reductive esterification of the ketone occurs (*260*). Hydrogen transfer to α,β-unsaturated ketones has been studied, and reduction of either the olefinic moiety (*274*) or the ketone function (*301*) has been observed. The hydrido complex $[IrHCl_2(S\text{-}Me_2SO)_3]$ reacts with the unsaturated ketone chalcone, PhC(O)CH:CHPh, to yield an isolable complex containing a coordinated 2-benzoyl-1-phenylethyl moiety (*271*). Crystal structure data (*392, 393*) clearly show the interaction between the organic substrate and the metal center. Acid hydrolysis of this complex yields dihydrochalcone (*274*).

A similar system based on rhodium has been studied (*123*) and was found to be less active than the equivalent iridium catalysts. Selective hydrogenation of acetylenes to olefins and dienes to monoolefins can be performed using the rhodium system, and the authors note that although propan-2-ol is an effective source of hydrogen (via oxidation to acetone), mild pressures of hydrogen gas can also be employed.

b. Activation of Molecular Hydrogen. Activation of molecular hydrogen in the reduction of Me_2SO to Me_2S has previously been mentioned (Section IV,C), and in conjunction with this several complexes of the platinum metals have been examined as catalysts for the reduction of unsaturated organic substrates. The action of molecular hydrogen on

Me_2SO solutions of ruthenium(III) salts has been described (*304*), and the ruthenium(II) complex $[NH_2Me_2][RuCl_3(S\text{-}Me_2SO)_3]$ found to be an effective catalyst precursor for the hydrogenation of acrylamide and ethyl vinyl ketone under mild conditions (*305*). The arene complex, $[Ru(C_6H_6)Cl_2]_2$, although active for the hydrogenation and isomerization of pent-1-ene at 30°C and 30 atmospheres of H_2 in dimethylformamide solution, is totally inactive in Me_2SO solution. In the absence of olefin and hydrogen, the complex $[Ru(C_6H_6)(Me_2SO)Cl_2]$ may be isolated, and this water-soluble complex is a catalyst for the hydrogenation of maleic acid at 25°C and 20 atmospheres of H_2. A hydrido complex, believed to be $[RuH(Cl)(C_6H_8)(Me_2SO)]$, may be isolated by treating an aqueous solution of $[Ru(C_6H_6)(Me_2SO)Cl_2]$ with hydrogen in the presence of triethylamine (*285*).

Attempts to use palladium(II) sulfoxide complexes alone as homogeneous hydrogenation catalysts have largely been unsuccessful. Thus, $[Pd(S\text{-}Me_2SO)_2Cl_2]$ is not a catalyst for the hydrogenation or isomerization of simple olefins (*206*). Reduction of the complex using sodium borohydride yields homogeneous solutions which are active in the hydrogenation of 1,3-pentadiene and cyclopentadiene and in the isomerization of allylbenzene (*206*). Studies using solutions stabilized by polyvinylpyrrolidine or supported on alumina have been reported and patented (*201, 206*). Using solutions of the reduced palladium sulfoxide catalyst, the olefinic moieties of $CH_2{:}CHCH_2OH$ and $CH_2{:}CHCH_2NH_2$ may be hydrogenated. The hydrogenation of the unsaturated amine is ~20 times as rapid as that of the unsaturated alcohol (*202*). The same system has been extensively studied as an isomerization catalyst (*200*) and as a selective catalyst for acetylene hydrogenation (*203*). Reports on a related system derived from the reduction of $[Rh(S\text{-}Me_2SO)_2(O\text{-}Me_2SO)Cl_3]$ by sodium borohydride have also appeared (*204, 205*). In addition to the activation of molecular hydrogen toward the reduction of organic substrates, these "reduced" palladium and rhodium dimethyl sulfoxide systems are catalysts for oxidation of hydrogen by molecular oxygen.

c. *Asymmetric Hydrogenation.* A subdivision of the topic of molecular hydrogen activation is the subject of asymmetric synthesis. Chiral sulfoxides coordinated to an active metal center seem suitable ligands to induce asymmetric hydrogenation, as the asymmetrically ligated atom is the donor (in *S*-sulfoxide complexes) and the pronounced trans influence of the sulfoxide moiety permits cis coordination of a prochiral olefin (see Section IV,A). Detailed ^1H-NMR studies of complexes of the type *cis*-[Pt(RR'SO)(olefin)Cl_2] (RR'SO = *p*-tolylmethyl sulfoxide; olefin = ethylene, propene, 1-butene, *cis*-but-2-ene, *trans*-but-2-ene, etc.) have been performed (*86*) in order to determine the extent to which chiral sulfoxides are capable of distinguishing between the prochiral faces of coordinated olefins. In general, the amount of chiral induction was found to be small.

The James group has synthesized a number of interesting chiral sulfoxides, including the potentially bidentate ligands meso-1,2-bis-(methylsulfinyl)ethane, (*R*,*R*)-1,2-bis(*p*-tolylsulfinyl)ethane, and (−)-(2*R*,3*R*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(methylsulfinyl)butane (*302*), the latter compound being the sulfoxide analog of the familiar chiral "diop" ligand (*300*). Ruthenium complexes of the type $[RuL_2Cl_2]_3$ (L = monodentate chiral sulfoxide) have been synthesized (*308*), and a polymeric complex $[RuL_2Cl_2]_n$ obtained for the racemic methyl phenyl sulfoxide ligand. Infrared and ^{1}H-NMR studies were unable to determine unambiguously the mode of coordination of the sulfoxide donors in these complexes. Ruthenium(II) complexes of the chelating sulfoxides have also been synthesized (*300*).

The use of these complexes as catalyst precursors for asymmetric hydrogenation has met with mixed results. Kinetic studies on the hydrogenation of acrylamide (70°C, 1 atmosphere H_2) using the catalyst precursor $[RuL_2Cl_2]_3$ [L = (+)-(*S*)-2-methylbutyl-(*S*,*R*)-methylsulfoxide] shows a dependence on ruthenium of one-third, implying that the active catalyst is a monomeric species. This trimeric species was an active precursor for the asymmetric hydrogenation of the terminal olefins 2-acetamidoacrylic and itaconic acids (*308*). The hydrogenation of itaconic acid to *R*-methylsuccinic acid was effected with a 15% enantiomeric excess (ee), whereas several trisubstituted olefins (for example, α- and β-methylcinnamic acids) were not hydrogenated at all. The analogous trimer of (+)-(*R*)-methyl-*p*-tolylsulfoxide facilitated the hydrogenation of activated olefins, including chiral olefins, but as reduction to ruthenium metal occurs concomitantly and hydrogenation is probably heterogeneous, no induction was observed. A comparison of the ability of chiral phosphine and chiral sulfoxide complexes of ruthenium (*308*) suggests that the former are generally the more effective in asymmetric synthesis.

Similar studies have been performed on rhodium(I) complexes of monodentate and potentially chelating sulfoxides (*301, 307*), again with rather mixed results. Complexes of the type $[Rh(diene)(PPh_3)(sulfoxide)]^+$ have been synthesized (*302, 306*) for a range of chiral sulfoxides where coordination appears to be via oxygen, but attempts to asymmetrically hydrogenate itaconic acid using these precursors were unsuccessful as disproportionation, as in Eq. (34), and subsequent catalysis by the bis(phosphine) system occurs (*302*).

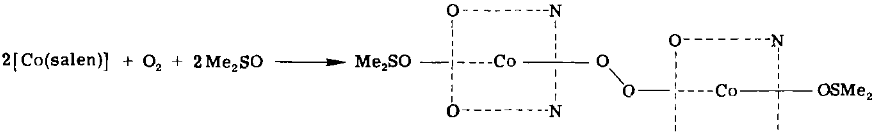
$$2[\mathrm{Rh(diene)(PPh_3)(sulfoxide)}]^+ \rightleftharpoons [\mathrm{Rh(diene)(PPh_3)_2}]^+ + [\mathrm{Rh(diene)(sulfoxide)_2}]^+ \quad (34)$$

In addition, it has been observed that iridum complexes generated *in situ* from $[\mathrm{IrCl_3{\cdot}3H_2O}]$ and chiral sulfoxides cause no asymmetric induction during hydrogenation (*300*).

F. Bioinorganic Chemistry of Sulfoxide Complexes

A review article has appeared (*237*) which discusses the biological activity of thioethers and their derivatives with particular reference to interactions with transition-metal ions. Accordingly, only some of the more salient points will be discussed here. In any biological studies, the toxicity of Me_2SO (*482*) and of its transition-metal complexes (*140*) should be borne in mind.

Some indication that transition-metal sulfoxide complexes are capable of acting as oxygen carriers is suggested by the ability of such complexes to undergo oxygenation and deoxygenation reactions (Sections IV,C and D). Accordingly, studies of complexes such as [Co(salen)] (salen = *N,N'*-ethylenebis{salicylideneimato}—) as oxygen carriers in the presence of donor solvents, such as dimethyl sulfoxide, have been performed (*98*). The results suggest that oxygen uptake occurs via formation of a dimeric complex, as shown in Eq. (35).



(35)

The dioxygen ligand is said to be stabilized by the presence of strong σ-donors in the trans position. Such complexes are of specific interest as models of the active myoglobin center (*473*). Preliminary reports of a related copper(II) system have appeared (*286*). Studies on the effect of extraplanar Me_2SO coordination on phthalocyanine derivatives of cobalt (*109*) and iron (*315–317*) have been performed and show that, for example, the low-spin d^6 iron(II) phthalocyanine complex dissolves in Me_2SO to give a diamagnetic blue solution which may be reacted further with donors such as imidazole, effecting replacement at the axial sites (*62*).

Studies on the anticarcinogenic chemotherapeutic effects of platinum(II) complexes (*487*) have suggested the possibility that activity is due to complexation with the purine and pyrimidine bases of deoxyribonucleic acid. A structural analysis of the complex *trans*-$[PtCl_2(iPr_2SO)(\mu\text{-9-methyladenine-}N^1,N^7)]$ has shown that coordination can occur via the N(1) and N(7) positions of the purine base, adenosine (*375*). The structural data suggest that analogous coordination to a coiled deoxyribonucleic acid chain will result in a marked structural distortion. Such distortion will of course have a noticeable effect on replication. It is also pertinent that, although complexes of the platinum metals, with the exception of platinum itself, generally show little antitumor activity, studies on the rhodium(III) complex $[Rh(S\text{-}Me_2SO)(pyridine)_2Cl_3]$ have shown it to be remarkably active against KB carcinoma (*in vitro*) and P388 leukemia (in mice). A structural study of this complex has been reported (*122*). The ability of platinum(II) dimethyl sulfoxide complexes to coordinate to nucleic acids has also found application in specific base sequence determination by electron microscopy (*422*). Studies of amino acid complexes of platinum(II), with particular reference to their interactions with Me_2SO, have been performed (*9, 175*). The interaction of Me_2SO with complexes of the type $[K][Pt(\overset{\frown}{N\ O})Cl_2]$ ($\overset{\frown}{N\ O}$ = bidentate amino acid coordinated via O and N) can yield either *cis*- or *trans*-$[Pt(\overset{\frown}{N\ O})(S\text{-}Me_2SO)Cl]$ complexes (*9*). Studies on related systems, such as $[Pt(An)(S\text{-}Me_2SO)Cl]$ (AnH = α-alanine) have shown that the sulfoxide is coordinated trans to the carboxylate moiety (*252*). Similar studies on sulfoxide complexes of biologically active heterocyclic amines (*354*) and on complexes of biologically significant thioether carboxylic acids and their sulfoxide derivatives (*236*) have also appeared.

V. Sulfoxide Complexes of the Transition Metals

An excellent review article (*460*) has covered much of the literature concerning Me_2SO complexes of the transition metals up to 1969. In consequence, only the major points prior to this period will be discussed, together with more recent developments and comments on complexes of the higher sulfoxides.

A. TITANIUM, ZIRCONIUM, AND HAFNIUM

A review on the chemistry of low-valent titanium has appeared which deals with some aspects of the chemistry of titanium sulfoxide complexes (*397*). Titanyl complexes of the type $[TiOL_5][ClO_4]_2$ have been prepared [L = Me_2SO (*336*), L = Ph_2SO (*431*)], and infrared studies imply *O*-bonding. Attempts to perform thermal analysis on the Me_2SO complex were unsuccessful, as an explosion occurred at 190°C. Conductivity studies on the Ph_2SO complex imply that the perchlorate moieties are ionic, rather than coordinated. Adducts of the titanium halides have been prepared, including [$TiCl_4 \cdot 11Me_2SO$], [$TiBr_4 \cdot 11Me_2SO$] (*474*), and [$TiF_4 \cdot 2Me_2SO$] (*170*). The ^{19}F NMR of the latter complex was also reported. Titanium(IV) alkoxychloride adducts of the type [$TiCl_2(OR)_2 \cdot (Me_2SO)$] (R = Me, Et, *i*Pr, *i*Bu, *n*Bu) have been reported (*106*), and a tentative alkoxy-bridged dimeric structure proposed. Infrared data imply *O*-bonding in these complexes. Zirconium chloride adducts of Me_2SO containing varying amounts of the sulfoxide have been prepared, including [$ZrCl_4 \cdot n(Me_2SO)$] [$n = 2, 3$ (*386*); $n = 8$ (*226*); and $n = 11$ (*474*)]. The higher solvates undoubtedly contain Me_2SO of crystallization, and this is indicated in the infrared spectra of the complexes (*226*). The bromide adducts [$ZrBr_4 \cdot n(Me_2SO)$] [$n = 2$ (*386*) and $n = 10$ (*474*)] have also been reported. The zirconyl complexes [$ZrOL_6$][ClO_4]$_2 \cdot n$L [L = Me_2SO, $n = 2$ (*338*); L = Ph_2SO, $n = 10$ (*431*)] and [$ZrOCl_2 \cdot Me_2SO$] (*436*) have been assigned as *O*-bonded from infrared data. Similarly, infrared data suggest that the cyanate complex [$Zr(OCN)_4(Me_2SO)_2$] is *O*-bonded (*117*).

The hafnium halide adducts [$HfX_4 \cdot n(Me_2SO)$] [X = Cl, Br; $n = 2$ (*386*); X = Cl, $n = 8$ (*226*); X = Cl, $n = 9$; X = Br, $n = 10$ (*474*)] have been prepared. In common with the cyanate complex [$Hf(OCN)_4(Me_2SO)_2$] (*117*), infrared data imply *O*-bonding in these compounds.

The use of sulfoxides in the separation of zirconium and hafnium has met with some success, and diheptyl sulfoxide has been patented as an extractant for this purpose (*185*). Mixtures of sulfoxides have also been used in the extraction of zirconium and hafnium from acid solutions (*463*).

B. Vanadium, Niobium, and Tantalum

The ability of vanadium(II) chloride to facilitate sulfoxide deoxygenation has been discussed (Section IV,C), and it appears that vanadium(III) sulfoxide complexes may be prepared by air oxidation of vanadium(II) salts in the presence of the sulfoxide. In this manner, [$V(Me_2SO)_6$][ClO_4]$_3$ was prepared from vanadium(II) perchlorate (*119*) and the kinetics of substitution with thiocyanate ion detailed. Care is necessary in handling the pure compound, as it is reported to be sensitive to detonation. A large number of oxovanadium(IV) species have been synthesized of the general type [VOX_2L_n] (X = anionic ligand, L = sulfoxide). Chloro complexes with two (*280*), two and one-half (*168*), and three (*436*) molecules of Me_2SO per metal center have been described. The bromide and iodide complexes [$VOX_2(Me_2SO)_5$] (*263, 415*) have also been synthesized. The synthetic difficulties in preparing complexes of the VIO_2— moiety may be overcome by electrolytic reduction of [$VOCl_3$] in alcoholic hydrochloric acid followed by metathetical exchange with potassium iodide (*263*). The complexes [$VO(R_2SO)_5$][ClO_4]$_2$ [R = Me (*430*); R = Ph (*431*)] have been shown to contain *O*-R_2SO ligands and noncoordinated perchlorate ions by a variety of analytical techniques. Oxalate and acetylacetonate vanadyl complexes are known to form adducts with various sulfoxides of the types [$VO(oxalate)(Me_2SO)_2$] (*429*) and [$VO(acac)_2(R_2SO)$] (R = Me, Et, *n*Pr, *n*Bu, etc.) (*297*). The latter complexes are of interest as a related system based on [$VO(acac)_2Cl$] in Me_2SO solution is an effective photoinitiator for free-radical polymerization reactions (*10*).

The reactions of [MX_5] (M = Nb, Ta; X = Cl, Br) with Me_2SO to yield [MOX_3(*O*-$Me_2SO)_2$] complexes have been discussed (Section IV,C) and the anomalous reaction of the fluorides [MF_5] (M = Nb, Ta) to yield [MF_5(*O*-$Me_2SO)_2$] mentioned. The ^{19}F-NMR spectrum of [TaF_5] has been recorded in Me_2SO solution and suggests that the species [$TaF_5(Me_2SO)$] is present (*97*). The corresponding reactions of [MX_5] (M = Nb, Ta; X = Cl, Br) with Ph_2SO in the presence of anhydrous alcohols (MeOH, EtOH) yields the alkoxy complexes [$M(OR)_2Cl_3(Ph_2SO)$]. Infrared data imply *O*-bonding of the sulfoxide (*57*). Organometallic complexes of the type [$CH_3MOX_2(Me_2SO)_2$] have been synthesized (M = Nb, Ta) via the action of a methyl Grignard reagent on [$MOCl_3$] and subsequent work-up in the presence of the sulfoxide (*465*). Infrared and ^1H-NMR data suggest *O*-bonding in these complexes. The oxalatoniobium complexes [M][$NbO(C_2O_4)_2(R_2SO)_2$] [M = NH_4, K, Rb, Cs; R_2SO = Me_2SO, $(CH_2)_4SO$] have been prepared, and spectroscopic data suggest the presence of a seven-coordinate niobium center (*90*). Sulfoxide adducts of the [Nb_6Cl_{12}]$^{2+}$ cluster have been isolated from [$Nb_6Cl_{14}\cdot 8H_2O$]. The complex [$(Nb_6Cl_{12})Cl_2\cdot(Me_2SO)_4$] is isolated by dissolution of the starting material in Me_2SO; further reaction with silver(I) perchlorate yields [$(Nb_6Cl_{12})(Me_2SO)_6$][ClO_4]$_2$, where the integrity of the central cluster is maintained (*192, 377*). A large amount of work has been reported on the use of sulfoxides in the extraction of niobium and tantalum, and patents exist for their use in this field (*379*). Separation of the elements by sulfoxide extraction from fluoride/sulfate solutions has been reported (*35*).

C. CHROMIUM, MOLYBDENUM, AND TUNGSTEN

Sulfoxide adducts of chromium, molybdenum, and tungsten carbonyls have been studied as catalysts for the polymerization of monomers such as vinyl chloride (*248*). Simple adducts of the type $[M(CO)_5(Me_2SO)]$ may be prepared by carbonyl displacement from the corresponding hexacarbonyl. Photochemical reactions are frequently necessary to cause carbonyl displacement; in this manner, many carbonyl complexes of higher sulfoxides have been prepared (*255, 256*). Infrared (*257*) and mass spectral studies (*154*) of these complexes have appeared, and infrared data suggest that *S*-bonding may occur in Cr(0) sulfoxide complexes, although definitive studies have not been reported.

A large number of Cr(III) sulfoxide complexes have been prepared as intermediates in the preparation of amine complexes for studies of Cr(III) solvolysis reactions. Thus, both cis and trans isomers of the complexes $[Cr(en)_2(X)(Me_2SO)]^{2+}$ [X = Cl (*186*); X = Br (*424*)] have been isolated. Similarly, *trans*-$[Cr(en)_2(Me_2SO)_2]^{3+}$ (*187*) and a related bipyridyl system (*215*) have also been studied. The solvolysis of $[Cr(H_2O)_6]^{3+}$ by Me_2SO is said to proceed via the $[Cr(H_2O)_n(Me_2SO)_{6-n}]^{3+}$ species (*31*), and the hexa(sulfoxide) complex, $[Cr(Me_2SO)_6]^{3+}$, has been isolated as its perchlorate salt (*405*). Infrared studies show the sulfoxide to be *O*-bonded. Thermal analysis results show the compound to be exceptionally stable up to 195°C (*221*), but further heating results in a violent explosion at 247°C (*405*). The labeled analog $[Cr(Me_2{}^{35}SO)_6][ClO_4]_3$ has also been prepared for use in substitution studies (*96*). The analogous nitrate salt, $[Cr(Me_2SO)_6][NO_3]_3$, has been prepared (*406*) and also shows exceptional thermal stability, retaining its integrity up to 160°C (*221*). Thiocyanate salts have been synthesized (*434*) for studies in solvolysis reactions (*374*), and the thermal behavior of these compounds examined (*53*). The halide complexes $[CrX_3(Me_2SO)_n]$ (X = Cl, $n = 3, 4, 5$; X = Br, $n = 6$ (*222, 438*) have been isolated and their thermal behavior studied.

The Cr(VI) complex, $[CrO_2Cl_2(Me_2SO)_3]$, has been reported, and infrared studies suggest *O*-bonding of the sulfoxide moiety (*436*).

In addition to the work on molybdenum carbonyl complexes previously mentioned where *S*-bonding has been postulated, the molybdenum oxyhalide complexes $[MoOCl_3(Me_2SO)_2]$ (*369*), $[MoO_2Cl_2(Me_2SO)_2]$ (*279*), and $[MoO_2F_2(Me_2SO)_2]$ (*249*) have been synthesized and infrared studies performed, which imply *O*-bonding of the Me_2SO ligand. A crystal structure determination of [$MoO_2Cl_2(Me_2SO)_2$] (see Table V) confirms *O*-bonding of the sulfoxide ligands. Several seven-coordinate molybdenum nitrosyl complexes of Me_2SO have also been reported (*92, 93*). Derivatives of the octa-μ_3-chlorohexamolybdate(II) cluster containing *O*-bonded Me_2SO have been prepared, including [$Mo_6Cl_8(Me_2SO)_6$][ClO_4]$_4$ (*126*) and [$(Mo_6Cl_8)Cl_4(Me_2SO)_2$] (*190*). The infrared spectra of these complexes imply coordination of the sulfoxide via oxygen and that the perchlorate moieties in the former complex are ionic, rather than coordinated.

Dimethyl sulfoxide has found application as a solvent for electrochemical studies of Mo(VI) and Mo(V) complexes of quinol derivatives (*287*). Sulfoxides have also been examined as extractants for the separation of molybdenum and tungsten from acid solutions (*218*).

D. MANGANESE, TECHNETIUM, AND RHENIUM

As in the case of chromium and tungsten, manganese carbonyl adducts of Me_2SO have been used as catalysts for the polymerization of vinyl chloride (*248*). Preparative studies have allowed the isolation of complexes of the type [$Mn(C_5H_4Me)(CO)_2(R_2SO)$] [$R_2SO$ = $(CH_2)_4SO$, $(CH_2O)_2SO$; see ref. *255*], and infrared (*257*) and mass spectral studies (*154, 275*) have appeared on these and related systems.

Manganese(II) complexes containing coordinated sulfoxides have been described in great detail; Me_2SO complexes (*95, 162, 362*), $(CH_2)_4SO$ complexes (*245*), $(PhCH_2)_2SO$ complexes (*497*), and complexes of the bidentate sulfoxides MeS(O)RS(O)Me [$R = (CH_2)_n$, $n = 2$, 3, 4] (*378*) have all been extensively discussed in the literature. Infrared studies (*64*) and magnetic susceptibility measurements (*209*) show that such complexes are high-spin with *O*-bonded R_2SO ligands. Manganese(II) thiocyanate (*489*) and selenocyanate (*67, 94*) sulfoxide complexes have been synthesized of the type [$Mn(Me_2SO)_4(NCX)_2$] (X = S, Se); all are reported to be six-coordinate, with *O*-bonded sulfoxide ligands and *N*-bonded thio- or selenocyanates.

Manganese(III) sulfoxide derivatives have also been reported, these complexes being active initiators in the polymerization of acrylonitrile (*153*). Both nitrate (*406*) and perchlorate (*426, 428*) complexes have been reported. In the infrared spectrum of [$Mn(Me_2SO)_6$][ClO_4]$_3$, two bands at 915 cm^{-1}(s) and 960 cm^{-1}(m) have been assigned as ν(S=O) and interpreted in terms of four strongly bound *O*-Me_2SO equatorial ligands and two weakly bound *O*-Me_2SO axial ligands.

No technetium complexes of sulfoxides have been reported. Mononuclear rhenium(V) complexes of the types [$ReO_2Cl(Me_2SO)$] (*246*) and

$[ReOCl_3(Me_2SO)]$ (*371, 372*) have been prepared, and infrared data suggest *O*-bonding of the sulfoxides. The high trans effect of the nitrosyl group in the complex $[Re(NO)X_5][NEt_4]_2$ (X = Cl, Br) allows replacement of a halide ligand by dimethyl sulfoxide to yield $[Re(NO)X_4(Me_2SO)][NEt_4]$. Upon heating, degradation occurs to yield $[Re(NO)X_4][NEt_4]$ (*120*). Trinuclear rhenium complexes, such as $[Re_3Cl_9(Me_2SO)_3]$ (*253*) and $[Re_3X_3(R_2SO)_3]$ [X = Cl, Br; R = Me; X = Cl; $R_2SO = Ph_2SO$, $(CH_2)_4SO$, etc.] (*133*), have been reported. The trinuclear rhenium(III) cluster $[Re_3Br_3(AsO_4)_2(Me_2SO)_3]$ has been prepared as a route to solubilizing the cluster to allow its separation from silver chloride, a by-product during its preparation. Structural details are available (*130*). The dimeric dichloroacetato(dimethyl sulfoxide)rhenium complex has been synthesized, and preliminary structural details have appeared (*332*).

E. Iron, Ruthenium, and Osmium

Iron carbonyl sulfoxide complexes of the type $[Fe(CO)_4(R_2SO)]$ have been synthesized [$R_2SO = Me_2SO$, $(CH_2)_4SO$] photochemically from $[Fe(CO)_5]$ (*255*) and their infrared spectra discussed (*257*). The interaction of Me_2SO with the π-allyl complex $[Fe(CO)_3(\pi\text{-}C_3H_5)Cl]$ results in displacement of the allyl moiety and coordination of the sulfoxide (*339*). Simple salts of the type $[Fe(R_2SO)_6][X]_2$ [R = Me, X = BF_4 (*362*); R = $PhCH_2$, X = ClO_4 (*496*); R = Ph, X = ClO_4 (*469*)] have been studied by infrared spectroscopy, and the data show the R_2SO ligands are *O*-bonded. The Mössbauer spectra of the complexes $[Fe(R_2SO)_6][ClO_4]_2$ (R = Me, Ph) have also been reported (*469*).

Iron(III) complexes of empirical formula $[Fe(R_2SO)_2Cl_3]$ have been prepared and various halide-bridged structures proposed (for R = Ph, see ref. *427*); the crystal structure data available (for R = Me, see ref. *60*) show the structure to be $[Fe(Me_2SO)_4Cl_2][FeCl_4]$. ESR data (*197*) support the existence of $[FeCl_4]^-$ ions in solutions of $FeCl_3$ in Me_2SO. Simple salts of the type $[Fe(Me_2SO)_6][X]_3$ [X = NO_3 (*118*); X = Cl (*254*); X = ClO_4 (*391*)] have been synthesized; the perchlorate salt decomposes explosively at 250°C (*309*), whereas the nitrate salt was stable to thermal analysis (*221*). Iron(III) complexes of beta(keto)sulfoxides have been reported, and evidence of bidentate coordination via sulfoxide and keto oxygen donors presented (*83*).

Of particular note is the complex $[Fe(CN)_5(Me_2SO)]^{3-}$ (*216*), where the positive shift in $\nu(S{=}O)$ upon sulfoxide coordination [$\Delta\nu(S{=}O) = +15\ cm^{-1}$] is taken as indicative of coordination via sulfur. No structural data appear to be available for confirmation.

In ruthenium sulfoxide complexes, both *O*- and *S*-coordination of sulfoxides have been reported and the modes of coordination determined crystallographically (see Section II,A). Ruthenium(II) complexes such as $[NH_2Me_2][Ru(S\text{-}Me_2SO)_3Cl_3]$ and $[Ru(S\text{-}Me_2SO)_3(O\text{-}Me_2SO)Cl_2]$ have been isolated and analyzed by X-ray crystallography (Section II,A). The former complex has been isolated as both red and yellow isomers (*82*) and has found application as a source material for the preparation of many novel ruthenium(II) complexes (*180*). Both complexes have been utilized as homogeneous hydrogenation catalyst precursors (*304, 305*). A range of ruthenium(III) complexes have been synthesized, including $[Na][Ru(Me_2SO)_2Cl_4]$ (*82*), $[Ru(Me_2SO)_3Cl_3]$ (*217*), $[Ru(Me_2SO)_5Cl][Cl]_2$, and $[Ru(Me_2SO)_6][Cl]_3$ (*81*). Infrared data suggest both *O*- and *S*-bonding in the latter two complexes.

The oxidation of coordinated Et_2S to yield the ruthenium(II) complex $[Ru_2Br_6(NO)_2(O\text{-}Et_2SO)_2]$ has been discussed (Section IV,C) and the structure of the complex described (Section II,A). The complex $[RuCl_2(PPh_3)_2(CO)]$ will reversibly add Me_2SO to yield the complex $[RuCl_2(PPh_3)_2(CO)(O\text{-}Me_2SO)]$. The complex is assigned as *O*-bonded on the basis of spectroscopic data (*283*).

No sulfoxide complexes of osmium have been reported. Unsymmetrical dialkyl sulfoxides have been utilized in extraction studies, and methyl-4,8-dimethylnonyl sulfoxide has found application in the extraction of iron (*266*). Extraction of ruthenium from hydrochloric acid solutions by sulfoxides has been studied (*470*) and comparisons of sulfones, sulfoxides, and thioethers as extractants for nitrosoruthenium species reported (*441, 443*). Similar studies on the extraction of nitrosoosmium species have been reported (*442*).

F. COBALT, RHODIUM, AND IRIDIUM

Sulfoxide complexes of cobalt(II) salts of the type $[Co(R_2SO)_6][X]_2$ have been prepared for a wide variety of sulfoxide ligands [$R = Me$, $X = ClO_4$ (*461*); $R = Ph$, $X = ClO_4$ (*228*); $R = PhCH_2$, $X = ClO_4$ (*496*); $R_2SO = (CH_2)_4SO$, $X = ClO_4$ (*129*); $R_2SO = (CH_2)_5SO$, $X = ClO_4$, BF_4 (*243*)]. Infrared studies have shown *O*-bonding of the sulfoxides in all cases. In addition, nitrate (*406*), thiocyanate, selenocyanate (*94, 158*), and cyanamide (*329*) complexes of cobalt(II) containing *O*-bonded Me_2SO have been reported. Complexes of the chelating sulfoxides MeS(O)RS(O)Me [$R = (CH_2)_n$, $n = 2, 3, 4$ (*378*)] and the isomeric *cis*- and *trans*-trithiane dioxides (*413*) have been reported for a range of divalent metal ions, including cobalt(II).

For studies of substitution reactions of octahedral complexes, many cobalt(III) sulfoxide complexes of the types *cis*- and *trans*-$[Co(en)_2(O\text{-}Me_2SO)X]^{2+}$ have been synthesized [X = Cl (*115*); X = Br (*193*); X = NO_2, (*367*)]. Related systems with monodentate amine ligands (*387*) have also been studied. Investigations into sulfur dioxide/dimethyl sulfoxide systems as oxidants (*219*) have shown that cobalt(II) sulfite can be oxidized to the corresponding Me_2SO adduct of the pyrosulfate, as shown in Eq. (36).

$$[CoSO_3] \xrightarrow{Me_2SO/SO_2} [CoS_2O_7(Me_2SO)_6] \tag{36}$$

The reaction in Eq. (36) is postulated as proceeding via a $[CoS_2O_5]$ species. The problem of whether Co(III) sulfoxide complexes are high-spin or low-spin has been mentioned in relation to the bonding model proposed by Kukushkin and co-workers (*48*). Few workers have reported magnetic susceptibility data for these complexes, as they are intuitively expected to be low-spin with a diamagnetic ground state. In addition, several syntheses have been reported which start with Co(II) salts, and the possibility of obtaining a product containing Co(II), and hence exhibiting a magnetic moment, has been discussed previously (see Section III). A definitive study is necessary to shed further light on this problem.

Remarkably few rhodium(I) dimethyl sulfoxide complexes have been reported in the literature, and several have previously been mentioned as likely catalyst precursors for the activation of small molecules (Section IV,E). Triphenylphosphine is displaced from Wilkinson's catalyst, $[Rh(PPh_3)_3Cl]$, by Me_2SO to yield *trans*-$[Rh(PPh_3)_2(S\text{-}Me_2SO)Cl]$; the sulfoxide is assigned as *S*-bonded by infrared studies (*360*). Bromide and iodide analogs of this complex have been reported and the reaction with carbon monoxide, to yield *trans*-$[Rh(PPh_3)_2(CO)Cl]$, described. The carbonyl complex $[Rh(S\text{-}Me_2SO)_2(CO)Cl]$ has been reported (*370*), as has the diene complex $[Rh(COD)(O\text{-}Me_2SO)_2][BF_4]$ (*233*); the assignments as *S*- and *O*-bonded, respectively, were from spectroscopic data.

Several Me_2SO adducts of rhodium(II) of the general type $[Rh_2(OOCR)_4(Me_2SO)_2]$ have been synthesized (*284, 388*) and their thermal decomposition via a two-step loss of sulfoxide studied (*52*). In addition, Me_2SO adducts of rhodium(II) thioacetate (*46*) and thiobenzoate (*45, 47*) complexes have been reported. Coordination of the sulfoxide moieties via sulfur is reported on the basis of spectroscopic data.

Rhodium(III) sulfoxide complexes $[Na][Rh(Me_2SO)_2Cl_4]$ and $[Rh(Me_2SO)_3Cl_3]$ have been synthesized (*182*) and the infrared spectra of these and their d^6-Me_2SO analogs studied. The complexes are assigned as *trans-S,S* and *mer-S,S,O*, respectively, on this basis. Interaction of $[Rh(Me_2SO)_3Cl_3]$ with silver(I) perchlorate allows isolation of the complex $[Rh(Me_2SO)_5Cl][ClO_4]_2$. Infrared studies show both *O*- and *S*-Me_2SO ligands to be present, and as three sulfoxide moieties are easily replaced by halide ions, the complex is formulated as $[Rh(S\text{-}Me_2SO)_2(O\text{-}Me_2SO)_3Cl]^{2+}$ (*291*). The remaining halide ligand of this complex cannot be abstracted to yield $[Rh(Me_2SO)_6]^{3+}$, even using an excess of silver(I) salt (*291*), and so an alternative route was employed to isolate this product, as shown in Eq. (37).

$$[RhCl_3] \xrightarrow{KOH} [Rh(OH)_3] \xrightarrow{HBF_4} [Rh(BF_3)_3] \xrightarrow{Me_2SO} [Rh(Me_2SO)_6][BF_4]_3 \quad (37)$$

Infrared and halide-substitution studies indicated that the complex was $[Rh(S\text{-}Me_2SO)_2(O\text{-}Me_2SO)_4]^{3+}$ (*477*).

Of this range of chlorosulfoxide complexes, both *trans*-$[Rh(S\text{-}Me_2SO)_2Cl_4]^-$ and *mer*-$[Rh(S\text{-}Me_2SO)_2(O\text{-}Me_2SO)Cl_3]$ have been studied by X-ray crystallography (Section II,A), which confirms the modes of coordination. The diethyl sulfoxide analogs $[Na][Rh(Et_2SO)_2Cl_4]$ and $[Rh(Et_2SO)_3Cl_3]$ have been prepared (*327*) and the modes of coordination assigned as *S*,*S* and *S*,*S*,*O*, respectively.

Substitution reactions of rhodium(III) sulfoxide complexes with thioethers (*290*), amines (*347*), and halide ions (*230*) have been detailed and some organorhodium(III) sulfoxide derivatives described (*417*). A series of complexes of the type $[Rh(C_5Me_5)(solvent)_3]^{2+}$ have been prepared, including the tris(dimethyl sulfoxide) complex, and utilized as reactive intermediates for many preparative studies. The sulfoxide complex was shown to be totally *O*-bonded, both in the solid state and in solution, by spectroscopic techniques (*39, 381–384*). The iridium(I) complex $[Ir(PPh_3)_2(O\text{-}Me_2SO)(CO)][ClO_4]$ has been isolated and assigned as *O*-bonded by spectroscopic techniques (*121, 459*). The complex was obtained via a substitution reaction of the reactive intermediate $[Ir(PPh_3)_2(MeCN)(CO)]^+$.

Iridium(III) sulfoxide complexes have received particular attention as hydrogen transfer catalysts (Section IV,E), and the species *cis*- and *trans*-$[Ir(S\text{-}Me_2SO)_2Cl_4]^-$, $[Ir(S\text{-}Me_2SO)_3Cl_3]$, *mer*-$[Ir(S\text{-}Me_2SO)_2(O\text{-}Me_2SO)Cl_3]$, $[Ir(S\text{-}Me_2SO)_3Cl_2H]$, and $[Ir(S\text{-}Me_2SO)_3Cl(H)_2]$ have been isolated (*259*) for this purpose. The benzylacetophenone intermediate $[Ir(C_{15}H_{13}O)(S\text{-}Me_2SO)_2Cl_2]$ has been examined by X-ray crystallography and found to be *S*,*S*-bonded (*392, 393*). The organometallic complex $[Ir(C_5Me_5)(Me_2SO)_3]^{2+}$ has been isolated (*39, 381*) and is of particular interest as infrared and ^1H-NMR data indicate that both *S*- and *O*-bonding are present in the solid state, while all three sulfoxide ligands are *S*-bonded in solution. This is no doubt a consequence of the increased steric demand, due to crystal packing effects, which precludes total *S*-bonding in the solid state. The higher mobility in solution allows ligand orientation such that the preferred mode of bonding can occur.

Limited reports on substitution reactions of iridium(III) sulfoxide complexes are available, and some amine sulfoxide complexes have been synthesized (*368*).

Iridium(IV) sulfoxide complexes, including $[\mathrm{Ir}(S\text{-}\mathrm{Me_2SO})_2\mathrm{Cl_4}]$ and $[\mathrm{H}(\mathrm{Me_2SO})_2]_2[\mathrm{IrCl_6}]$ have been prepared; the former complex is assigned as *S*-bonded by spectroscopic data (*30*). Some work on the solvent extraction of rhodium and iridium during refining processes, which utilizes sulfoxides, has been reported (*416*).

G. NICKEL, PALLADIUM, AND PLATINUM

Reports of nickel(II) dimethyl sulfoxide complexes are extremely numerous; the species $[\mathrm{Ni}(\mathrm{Me_2SO})_6][\mathrm{X}]_2$ [$\mathrm{X} = \mathrm{BF_4}$ (*362, 363*); $\mathrm{X} = \mathrm{NO_3}$ (*405*); $[\mathrm{X}]_2 = [\mathrm{NiCl_4}]$ (*162, 238*)] have been isolated, and ^{1}H-NMR studies (*462*) and MCD studies (*264*) have appeared. In addition, $[\mathrm{Ni}(\mathrm{Me_2SO})_8][\mathrm{X}]_2$ complexes have been isolated [$\mathrm{X} = \mathrm{Cl}, \mathrm{ClO_4}, \mathrm{NO_3}$ (*221, 223*)] which undergo thermal degradation via $[\mathrm{Ni}(\mathrm{Me_2SO})_3\mathrm{Cl_2}]$ (which is probably $[\mathrm{Ni}(\mathrm{Me_2SO})_6][\mathrm{NiCl_4}]$ in reality) to $[\mathrm{Ni}(\mathrm{Me_2SO})\mathrm{Cl_2}]$.

Complexes of the ligands $(\mathrm{CH_2})_4\mathrm{SO}$ (*129*), $(\mathrm{CH_2})_5\mathrm{SO}$ (*243*), $\mathrm{Ph_2SO}$ (*241*), and $(\mathrm{PhCH_2})_2\mathrm{SO}$ (*497*) have been synthesized, and spectroscopic data indicate *O*-bonding in all cases. ^{1}H-NMR studies of $\mathrm{Ph_2SO}$ complexes, including those of nickel(II), have appeared (*498*).

Thiocyanate and selenocyanate complexes of the type $[\mathrm{Ni}(\mathrm{Me_2SO})_4(\mathrm{NCX})_2]$ have been reported; infrared studies of the thiocyanate complex (*102, 489*) imply that the sulfoxide moiety is *O*-bonded, but some doubt as to the mode of coordination of the thiocyanate anion is apparent. The selenocyanate analogs appear to contain $O\text{-}\mathrm{Me_2SO}$ and $N\text{-}\mathrm{NCSe^-}$ ligands (*67, 94*). The dicyanamide complex of empirical formula $[\mathrm{Ni}(\mathrm{N}\{\mathrm{CN}\}_2)_2(\mathrm{Me_2SO})_2]$ is assigned a polymeric structure with bridging dicyanamide groups on the basis of infrared and magnetic susceptibility data (*329*).

Nickel(II) complexes of a variety of bidentate sulfoxide ligands have been reported (*326, 378, 413*) and $[\mathrm{NiL_3}][\mathrm{ClO_4}]_2$ species reported where L is the unusual bidentate ligand 2-(ethysulfinyl)pyridine-*N*-oxide. Bidentate *O,O*-coordination via sulfoxide and pyridine-*N*-oxide donors is assigned from infrared data (*63*).

Mixed neutral ligand nickel(II) sulfoxide complexes $[\mathrm{Ni}(\widehat{\mathrm{L\;L}})(\mathrm{Me_2SO})_2]^{2+}$ have been synthesized [$\widehat{\mathrm{L\;L}}$ = 1,4,7,11-tetraazaundecane (*124*); $\widehat{\mathrm{L\;L}}$ = 1,2-diphenylethylenediamine (*227*); $\widehat{\mathrm{L\;L}}$ = acetylacetonate, (*26*)], largely for use in kinetic studies of substitution reactions. The complex $[Ni(en)_3][BPh_4]_2 \cdot 3Me_2SO$ has been isolated, but a crystallographic study (*136*) shows that there is no bonding interaction between the metal center and the sulfoxide. The oxidizing system based on sulfur dioxide and dimethyl sulfoxide previously mentioned has been used to synthesize the pyrosulfate complex $[Ni(Me_2SO)_6][S_2O_7]$ (*219*).

Much of the chemistry of palladium and platinum sulfoxide complexes has been discussed in previous sections and so only additional salient points will be mentioned here. A complete listing of all palladium and platinum sulfoxide complexes prepared would require a review article in itself.

A noteworthy novel preparative technique has been developed for the synthesis of $[Pt(S\text{-}Me_2SO)_2Cl_2]$ from the reactive intermediate $[Pt(IPh_2)_2Cl_4]$; the by-products here are ultimately chlorobenzene and iodobenzene (*334*). Some problems were initially observed in the synthesis of $[M(S\text{-}Me_2SO)_2Cl_2]$ (M = Pd, Pt) by conventional means, as the original syntheses (*127*) were found to be somewhat irreproducible (*357*).

Platinum(IV) species have been conveniently synthesized from the reaction between halogens and platinum(II) sulfoxide complexes (*6*). Studies of the redox properties of such complexes show that they have a particularly high redox potential. Thus, the redox potentials for Eq. (38) are 0.872 V (R = Me) and 0.877 V (R = Et), measured at 25°C (I = 0.1 M). For comparison, the equivalent redox potential for $[Pt(pyridine)Cl_5]^-$ is 0.809 V (*349*).

$$[Pt(S\text{-}R_2SO)Cl_5]^- + 2e^- \rightleftharpoons [Pt(S\text{-}R_2SO)Cl_3]^- + 2Cl^- \qquad (38)$$

Undoubtedly, one of the major interests in platinum-metal sulfoxide chemistry is the synthesis and use of O-bonded sulfoxide complexes as reactive intermediates in synthetic and catalytic chemistry. The chemistry of such weakly bonded intermediates has recently been reviewed (*142*).

Studies on the use of sulfoxides as extractants for these metals have been reported (*75, 457*).

H. COPPER, SILVER, AND GOLD

Copper(II) dimethyl sulfoxide complexes $[Cu(Me_2SO)_n]^{2+}$ [n = 4 (*309, 391*); n = 5 (*496*); n = 9 (*221*)] have been synthesized and assigned as O-bonded by spectroscopic study. The Ph_2SO complex $[Cu(Ph_2SO)_4]^{2+}$ (*228*) has been prepared and isolated as its perchlorate salt. Preliminary crystallographic data (*320*) and ESR data (*483*) are available which suggest D_{4h} symmetry for the metal-ion site.

Copper(II) complexes of the ligands $(CH_2)_4SO$ (*129*), $(CH_2)_5SO$ (*243*), MeS(O)RS(O)Me [R = $(CH_2)_n$, $n = 2, 3, 4$ (*378*)], PhS(O)RS(O)Ph [R = $(CH_2)_n$, $n = 1, 2$ (*326*)], and trithiane dioxide (*413*) have also been reported.

The complex $[Cu(O\text{-}Me_2SO)_2Cl_2]$ has been examined by X-ray crystallography (see Section II,A) and studies made of its magnetic properties (*268, 404*).

Dimethyl sulfoxide adducts of copper(II) carboxylate complexes have been synthesized and binary $[Cu_2(Me_2SO)_2L_4]$ species (*84, 402*) isolated. Infrared studies suggest that the sulfoxide is *O*-bonded. In addition, X-ray data have been presented for the adduct $[Cu(O\text{-}Me_2SO)_3(p\text{-}HOC_6H_4CO_2)_2]$ (*2*). Various silver(I) ion–dimethyl sulfoxide systems have been reported and the complexes $[Ag(Me_2SO)_n][X]$ [$n = 1, 2$; X = ClO_4, NO_3 (*7, 108, 425*)] synthesized. Thermometric (*299*) and stability (*262*) measurements on these systems have also been reported. Crystallographic data (Table V) have been reported which confirm *O*-bonding in these complexes. Various gold(III)–dimethyl sulfoxide systems have been investigated (*445, 446*), and both $[Au(Me_2SO)Cl_3]$ and $[H(Me_2SO)_2][AuCl_4]$ are isolable during preparative procedures. The latter complex may be a result of using only reagent-grade protic solvents in the synthesis (*446*). Dimethyl sulfoxide has found particular use as a solvent for electrochemical studies of gold(I) complexes, as disproportionation tends to occur in aqueous solution (*295*). Redox equilibria in dimethyl sulfoxide have also been examined (*135*). A comparative study of the use of thioethers, sulfoxides, and sulfones in the solvent extraction of gold(III) species has been reported (*17*).

I. ZINC, CADMIUM, AND MERCURY

Simple $[Zn(Me_2SO)_n][ClO_4]_2$ complexes [$n = 4$ (*95*); $n = 5$ (*139*); $n = 6$ (*127*)] have been isolated and shown by infrared studies to contain *O*-Me_2SO ligands. In addition, chloride (*220*), bromide (*1*), and iodide (*231*) complexes have been described and crystallographic data presented for the $[Zn(O\text{-}Me_2SO)_4Cl_2]$ complex (*211*). The selenocyanate complex $[Zn(Me_2SO)_4(NCSe)_2]$ has also been reported (*8*). The $(CH_2)_4SO$ complex $[Zn(\{CH_2\}_4SO)_{2.5}Cl_2]$ has been synthesized and its fractional formula explained in terms of a possible dimeric or polymeric structure (*66*). Cadmium(II) dimethyl sulfoxide complexes including chloride (*220*), bromide (*1*), and iodide (*231*) species have been reported. The isostructural complexes $[Cd(Me_2SO)_2(NCX)_2]$ (X = S, Se) have also been prepared (*366*). Separate studies of diphenyl sulfoxide and cyclic sulfoxide complexes of cadmium(II) have appeared (*105, 232*). In addition, the rather unusual heteropolynuclear solvates $[MHg_2I_6(Me_2SO)_8]$ (M = Cd, Pd) have been reported (*54*).

Mercury halide complexes have been mentioned as agents for the oxidation of coordinated thioethers to sulfoxides (Section IV,D). The proposed mechanism suggests that mercury(II) sulfoxide complexes are *O*-bonded and, although some suggestion has been made to the contrary (*228*), most available infrared data seem to suggest that *O*-bonding does occur. An analysis of infrared and Raman data of $[(RR'SO)_nHgCl_2]$ species (n = 1, 1.5, 2) shows excellent correlation with proposed halide-bridged structures (*77*), and shifts in $\nu(S{=}O)$ values (*11*) imply *O*-bonding of the sulfoxide ligands. Crystallographic data (Table V) confirm an *O*-bonded polymeric structure. A six-coordinate mercury(II) species $[Hg(Me_2SO)_6][ClO_4]_2$ has been isolated; this is noteworthy, as complexes of mercury(II) with oxygen donors are of low stability and so tend to exhibit low coordination numbers (*103*). More typically, Me_2SO is known to form a 1:1 adduct with $[Hg(C\{NO_2\}_3)_2]$ (*207, 208*).

J. SCANDIUM, YTTRIUM, THE LANTHANIDES, AND THE ACTINIDES

Isolable scandium Me_2SO complexes of the type $[Sc(Me_2SO)_6][X]_3$ have been reported [X = Br, ClO_4 (*138, 364*)], as has the rather unusual four-coordinate species $[Sc(Me_2SO)_4][X]_3$ (X = Cl) (*364*). The use of conductivity data to determine the ion type, and hence the coordination number of the central ion, is essential in the characterization of such complexes where expansion of the coordination number by coordination of the anionic ligands is possible. Thus, the complex $[Sc(Me_2SO)_3(NCS)_3]$ is a nonconductor in chloroform solution, and this implies that the metal center is six-coordinate and that coordination of the anionic ligands has occurred (*137*). Scandium complexes of Ph_2SO (*169*) and of cyclic sulfoxides, such as $(CH_2)_4SO$, have also been reported (*150*). In all cases, coordination of the sulfoxides is accompanied by a decrease in $\nu(S{=}O)$, implying *O*-bonding to the metal center.

Studies of the lanthanide series, usually taken to include yttrium, have been made, and complexes of the general formula $[M(R_2SO)_n][X]_3$ examined for various R and X groups.

Perchlorate complexes $[M(Me_2SO)_n][ClO_4]_3$ have been isolated (*335, 363*) and the variation in coordination number with the atomic number of M elucidated. Thus, for M = La, Ce, Pr, and Nd, n = 8; for M = Sm Eu, Gd, Tb, Dy, Ho, and Y, n = 7; and for M = Er, Tm, Yb, and Lu, n = 6. It can clearly be seen that the coordination number decreases as the atomic number increases, exactly as expected in terms of the so-called "lanthanide contraction." The use of cryoscopy and conductivity measurements clearly demonstrates that no anion coordination occurs in these complexes. Infrared spectroscopy suggests *O*-bonding of the sulfoxide ligands.

The characterization of the analogous $n\mathrm{Pr_2SO}$ complexes has proved to be more difficult (*55*). Analytical data suggested an empirical formula of $[\mathrm{M_2}(n\mathrm{Pr_2SO})_{11}(\mathrm{ClO_4})_6]$ (M = Gd, Dy, Er), and the molar conductivities in nitromethane solution implied the presence of a 2:1 electrolyte type. The infrared spectra of these complexes showed that *O*-bonded $n\mathrm{Pr_2SO}$ ligands and both coordinated and ionic perchlorate moieties were present. To account for these data, structures have been proposed where each metal center is coordinated to five sulfoxide ligands and one perchlorate ligand, with another sulfoxide moiety bridging the two metal centers. Each metal ion is therefore seven-coordinate on this basis, suggesting that the increased steric hindrance on passing from $\mathrm{Me_2SO}$ to $n\mathrm{Pr_2SO}$ is insufficient to cause a decrease in coordination number.

The complexes $[\mathrm{M(Ph_2SO)_6}][\mathrm{ClO_4}]_3$ (M = La, Ce, Pr, Nd, Sm, Gd, Ho, Yb, Y) have been isolated (*455*) and characterized. Conductivity measurements show the complexes to be 3:1 electrolytes in a range of solvents ($\mathrm{MeNO_2}$, $\mathrm{PhNO_2}$, MeCN, and $\mathrm{Me_2SO}$), and cryoscopy studies show that four species are formed in nitromethane solution while ten are formed in dimethyl sulfoxide solution. Solvolysis to yield a dimethyl sulfoxide complex in this manner suggests that the aliphatic sulfoxide is a better ligand for these metal ions. The high steric bulk of the $\mathrm{Ph_2SO}$ ligand is presumably the reason for the decrease in coordination number for the lighter elements, from seven or eight in the $\mathrm{Me_2SO}$ analogs to six in the $\mathrm{Ph_2SO}$ complexes. Infrared data again suggest *O*-bonding. It is noteworthy that some workers have attempted to synthesize these $[\mathrm{M(Ph_2SO)_6}][\mathrm{ClO_4}]_3$ complexes (*478*) and obtained instead seven-coordinate $[\mathrm{M(Ph_2SO)_7}][\mathrm{ClO_4}]_3$ (M = Sm, Eu, Yb) species. The $\mathrm{(CH_2)_4SO}$ complexes $[\mathrm{M(\{CH_2\}_4SO)}_n][\mathrm{ClO_4}]_3$ have been synthesized and also show a decrease in coordination number with increasing atomic number; thus, for M = La, Ce, Pr, Nd, Sm, Eu, and Gd, $n = 8$; for M = Tb, Dy, Ho, Er, and Y, $n = 7.5$; for M = Tm, Yb, and Lu, $n = 7$ (*491*). For the cases where $n = 7.5$, a structure is proposed where one sulfoxide moiety lies in an intermediate position between two metal ions, similar to that mentioned for the $n\mathrm{Pr_2SO}$ complexes above. Thioxane oxide complexes of the type $[\mathrm{M(ligand)}_n][\mathrm{ClO_4}]_3$ have been prepared (for M = La, Ce, Pr, and Nd, $n = 9$; for M = Sm, $n = 8.5$; for M = Eu, Gd, Tb, Dy, Ho, and Er, $n = 8$; for M = Tm, Yb, Lu, and Y, $n = 7$), and also demonstrate this effect (*439*). The conductivity data of these complexes are rather unusual as they suggest the presence of 2:1 electrolytes in nitromethane solution; this is explained in terms of ion-pairing effects. Lanthanide perchlorate complexes of other cyclic sulfoxides, including 1,4-dithianemonosulfoxide (*412*) and *trans*-1,4-dithiane-1,4-dioxide (*411*), have also been prepared. The complexes of the latter, potentially chelating, sulfoxide are of interest as the infrared spectra suggest that the ligand is functioning, at least partly, as a unidentate donor. The insolubility of the complexes prevents total characterization.

Hexafluorophosphate derivatives, such as $[M(Me_2SO)_n][PF_6]_3$ (M = La, Lu, Y), have been synthesized (*365*), and infrared data show *O*-bonding of the sulfoxide with ionic hexafluorophosphate groups. Analytical data are incomplete for this series, as decomposition, postulated to be to lanthanide fluorides, occurs. The $(CH_2)_4SO$ complexes $[M(\{CH_2\}_4SO)_{7.5}][PF_6]_3$ are reported (*145*), which are 3:1 electrolytes with uncoordinated anions, implying a possible semibridged structure, as previously mentioned. Complexes of other cyclic sulfoxides, including thioxane oxide (*146*) and *trans*-1,4-dithiane-1,4-dioxide (*147*) derivatives of hexafluorophosphate salts have also been prepared.

With more powerful anionic ligands, such as nitrate, the situation becomes more interesting as there is a very real likelihood of anion coordination. Isolable complexes $[M(Me_2SO)_n(NO_3)_3]$ (for M = La, Ce, Pr, Nd, Sm, and Gd, $n = 4$; for M = Ho, Yb, and Y, $n = 3$) have been studied by infrared spectroscopy (*451, 453*), which shows *O*-bonding of the sulfoxides and suggests the presence of a single coordinated nitrate group. X-Ray crystallographic studies (Table V) contradict this, showing that the nitrate groups are all chelating and that the coordination numbers are nine and ten. The decrease in coordination number with increasing atomic number has again been explained in terms of the lanthanide contraction (*71*) and the infrared data reinterpreted in terms of the known structures (*324*). Lanthanide nitrate complexes of thioxane oxide (*212*), nPr$_2$SO (*56*), and tetramethylene sulfoxide (*492*) have also been described. Sulfoxide complexes of the lanthanide chlorides, $[M(Me_2SO)_nCl_3]$ (for M = La, Ce, Pr, Nd, Sm, and Gd, $n = 4$; for M = Y, $n = 3$), have been prepared which are nonelectrolytes in acetonitrile solution (*452, 454*), indicating coordination numbers of six and seven for the metal center. Lanthanide chloride complexes of cyclic sulfoxides have also been examined (*467*).

Dimethyl sulfoxide complexes of the lanthanide bromides $[M(Me_2SO)_8Br_2][Br]$ have been isolated (*480*), which are 1:1 electrolytes in acetonitrile solution, indicating a coordination number of ten.

The coordinating ability of halide ions toward formation of coordinate bonds with lanthanide ions lies in the order F >> Cl > Br > I, as expected with typical "hard" metal ions (*437*). The coordination number would therefore be expected to increase in the order I > Br > Cl > F, on the basis of electroneutrality. The coordination numbers of dimethyl sulfoxide complexes of lanthanide chlorides are six or seven, while for the lanthanide bromide complexes the coordination number is ten. Comparable iodide complexes may be expected to exhibit higher coordination numbers, but this is not observed and it is postulated that the large size of the iodide ligand sterically prevents expansion of coordination number (*331*).

In addition to these systematic studies of lanthanide sulfoxide complexes, with variation in both sulfoxide and anion, other more isolated reports are available. Lanthanide isothiocyanate complexes of the cyclic sulfoxides thioxane oxide (*490*) and tetramethylene sulfoxide (*493*) have been synthesized and complexes of the unusual potentially chelating ligand 2-(ethylsulfinyl)pyridine-*N*-oxide (*63*) described. Detailed studies of the solvation of lanthanide-shift reagents by Me_2SO have also appeared (*178, 179*).

Studies on the use of sulfoxides in the extraction of scandium (*325, 440*), yttrium (*188*), and the lanthanide series (*456*) have all been reported and seem to show considerable promise.

Studies on sulfoxide complexes of the actinide series have concentrated largely on the chemistry of thorium(IV), uranium(IV), and uranium(VI), although some reports of sulfoxide complexes of the remaining actinides have appeared. The thorium(IV) perchlorate adduct $[Th(Me_2SO)_{12}][ClO_4]_4$ has been isolated (*336*); it undergoes thermal degradation to yield $[Th(Me_2SO)_6][ClO_4]_4$ by loss of lattice-held molecules of Me_2SO. Infrared (*336*) and preliminary X-ray crystallographic data (*338*) are available, and some suggestion has been made that thermal degradation may be accompanied by a change in mode of coordination of the sulfoxide (from *O*- to *S*-bonded).

Reports of Me_2SO adducts of thorium(IV) chloride are inconsistent in the formulation of the product. Thus, $[Th(Me_2SO)_5Cl_4]$ (*38*), $[Th(Me_2SO)_6Cl_4]$ (*58*), and $[Th(Me_2SO)_7Cl_4]\cdot 3H_2O$ (*294*) have all been proposed as products. The thermal decomposition of thorium(IV) chloride dimethyl sulfoxide adducts has been reported (*37*).

Similarly, thorium(IV) bromide adducts of the general formula $[ThBr_4(Me_2SO)_n]mH_2O$ [$n = 1, m = 4$; $n = 10, m = 1$; $n = 8, m = 1$; $n = 6, m = 0$ (*58*); $n = 4, m = 4$; $n = 6, m = 3$; $n = 8, m = 0$; $n = 10, m = 4.5$ (*293*)] have been described. Thermal decomposition is via initial loss of water, followed by loss of sulfoxide and oxidation to thorium(IV) oxide. Infrared studies show that coordination of the sulfoxide results in a shift to lower frequency of $\nu(S{=}O)$, implying coordination via oxygen.

Reports of nitrate (*40, 58*) and sulfate (*294*) adducts of Me_2SO have also appeared. An X-ray structure of the rather unusual complex $[ThL_4(Me_2SO)]\cdot Me_2SO$ (HL = 8-hydroxyquinoline) has appeared which shows the presence of a nine-coordinate thorium ion, with one *O*-bonded and one lattice-held dimethyl sulfoxide moiety. No details of the geometry of the dimethyl sulfoxide unit are reported due to inverse overlap, a consequence of the centrosymmetric arrangement of the ThL_4 unit in the crystal lattice (*479*).

A study of thorium(IV) Ph_2SO complexes (*432*), using the conductometric method to determine the coordination number, shows that in complexes of the type $[ThX_4]\cdot nPh_2SO$ the coordination number varies with anion; the perchlorate complex $[Th(Ph_2SO)_6][ClO_4]_4$ is six-coordinate, $[Th(Ph_2SO)_4X_4]$ (X = Cl, Br, NCS) are eight-coordinate, as is the ionic complex $[Th(Ph_2SO)_6I_2][I]_2$, while the nitrate complex $[Th(Ph_2SO)_3(NO_3)_4]$ appears to be 11-coordinate with four bidentate nitrate donors. Other preparative reports (*450, 481*) appear to substantiate these results. A separate study of Ph_2SO and Et_2SO adducts of actinide nitrates (*14*) has been performed and a range of $[M(NO_3)_4]\cdot nR_2SO$ (M = Th, U, Np, Pu) complexes isolated. Although a decrease in coordination number with increasing atomic number or with increasing steric bulk of the sulfoxide would be expected, as for the lanthanide series, the results reported are insufficient to confirm this and further work is necessary for clarification. Uranium(IV) chloride adducts $[UCl_4(Me_2SO)_n]$ have been prepared by interaction of $[UCl_4]$ and the sulfoxide. The adduct obtained initially ($n = 7$) undergoes degradation *in vacuo* (to $n = 3$) (*38*). Other reports suggest that the $[UCl_4(Me_2SO)_3]$ adduct can be obtained directly (*40*), although a higher adduct, $[UCl_4(Me_2SO)_4]$, has also been reported (*420*). Characterization of such complexes is rather difficult as spectrophotometric and conductometric measurements (*167*) show that uranium(IV) halide–sulfoxide systems exist as a complex series of equilibria between a large number of neutral and ionic species. Attempts to use solution techniques to characterize an isolated solid may thus lead to errors in formulation.

Uranium(IV) chloride adducts of Ph_2SO have been isolated (*73*) of the type $[U(Ph_2SO)_2Cl_4]\cdot nH_2O$, and infrared measurements show the sulfoxide to be *O*-bonded. Analogous complexes of diphenyl sulfone could not be synthesized (*251*).

The uranium(VI) system derived from $[UO_2(ClO_4)_2]\cdot 6H_2O$ and dimethyl sulfoxide is of particular interest; interaction at low temperatures (20°C) is reported to yield $[UO_2(O\text{-}Me_2SO)_4][ClO_4]_2\cdot Me_2SO$. Formulation is on the basis of infrared data, where two bands at 941 cm^{-1} and 1026 cm^{-1} are assigned as $\nu(S{=}O)$ of *O*-bonded and lattice-held Me_2SO, respectively. The ν_3 and ν_4 bands of the perchlorate moiety indicate tetrahedral symmetry and hence the presence of ionic perchlorate. Heating this complex to 170°C causes changes in the infrared spectrum, and only one band could be assigned as ν(S=O), at 1152 cm^{-1}. Although the ν_3 and ν_4 perchlorate bands are split, indicating interaction between the anion and metal center with a corresponding decrease in symmetry, the new complex is formulated as $[UO_2(S\text{-}Me_2SO)_4][ClO_4]_2$ (*337*). Such thermal isomerizations from *O*- to *S*-coordination have been proposed for other related systems (*vide supra*).

Many uranium(VI) sulfoxide complexes of the type $[UO_2X_2(Me_2SO)_n]$ (X = anionic ligand) have been synthesized, including chloride, bromide (*322, 323*), nitrate (*41*), and acetate (*431*) adducts. The thiocyanate (*113, 114*) and selenocyanate (*292*) adducts $[UO_2(XCN)_2(Me_2SO)_2]$ have been synthesized, and infrared data indicate the presence of *O*-Me_2SO and *N*-NCX ligands.

Diphenyl sulfoxide complexes of uranium(VI) have been reported (*495*) and a thorough infrared and conductivity study detailed (*433*), suggesting that the thiocyanate complexes of empirical formula $[UO_2(R_2SO)_2(NCS)_2]$ are in fact dimeric with bridging *N,S*-NCS ligands.

Studies of sulfoxide complexes of other actinide elements have appeared, (*38, 40*), but insufficient data are available to make any meaningful comparisons along the series. Work on the solvent extraction of actinide elements by sulfoxides has been reported (*423*).

VI. Conclusions

The ambidentate donor ability of sulfoxides makes them potentially useful ligands for nearly all metal ions, and, in consequence, reports of sulfoxide coordination compounds are extremely numerous. Nonetheless, the bulk of the work reported to date has involved synthetic procedures, and the problems in these are now largely overcome. The resulting syntheses are often relatively simple and thus present easy routes to an extremely wide range of metal complexes with differing properties resulting from variation in metal center, anionic ligand, or sulfoxide. The exploitation of this wide range of compounds in preparative chemistry, homogeneous catalysis, organic syntheses, and bioinorganic chemistry has only recently begun, and these fields will undoubtedly receive growing attention as the attraction of utilizing metal complexes of cheap, easily synthesized, and highly versatile ligands increases in the future.

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