633. *Reactions of Sulphoxides with Some Group III and IV Halides.*

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The reactions of certain sulphoxides (R_2 in R_2SO = Me_2, Pr^iBu^t, Bu^t_2, or Ph_2) with boron, silicon, or tin halides have been investigated. As a rule, molecular addition compounds were obtained, but anomalous behaviour was noted in certain cases (Me_2SO–BCl_3, Me_2SO–$SiCl_4$, and Ph_2SO–$SiCl_4$) to give chloro-substituted sulphides or their derivatives (including $Cl{\cdot}CH_2{\cdot}S{\cdot}CH_3,BOCl$). A self-consistent picture of sulphoxide–halide reactions is presented. The infrared spectra of the sulphoxides and their complexes have been investigated and detailed assignments are presented for the aromatic derivatives; structural and stereochemical implications are discussed and structure (II) is confirmed.

DIMETHYL SULPHOXIDE has been used extensively as a solvent, because it has been recognised as highly polar. Until recently, the properties of sulphoxides as ligands had not, however, been explored [apart from some early references to adducts of diaryl sulphoxides with cadmium iodide, chloroplatinic, chloroauric, and cyanoferrous acid,[1] and with iron(III) chloride [2]]. Several papers have appeared, within the last few months, on co-ordination compounds of dimethyl sulphoxide with transition-metal derivatives,[3,4] as well as with halides of certain representative elements [zinc chloride and bromide (also nitrate and perchlorate), cadmium chloride,[3] boron fluoride,[3a,5] aluminium chloride,[3a] silicon,[6a] germanium(IV), and tin(IV) fluorides, tin(IV) chloride,[3] and antimony-(III) and -(IV) chlorides [7]]; a 1 : 1 adduct of diphenyl sulphoxide and antimony(V) fluoride has also been prepared.[4] Dimethyl sulphoxide was said to form complexes with silicon tetrachloride and with trichlorosilane.[6b] This prompts us to present our results on the reactions of boron, silicon, and tin(IV) halides with dimethyl, isopropyl t-butyl, di-t-butyl, and diphenyl sulphoxides and on the infrared spectra of these sulphoxides and of certain of their complexes.

Dimethyl sulphoxide is clearly a powerful donor (although weaker in this respect than triphenylphosphine oxide or diphenyl selenoxide [7]) because of the wide range of compounds with which it forms molecular complexes. That it, unlike the sulphide or sulphone, formed a stable complex with boron trifluoride, led Laughlin [5] to suggest that the oxygen and not the sulphur was the donor atom. This was also the conclusion of Cotton and co-workers [3] with respect to some thirty-four complexes, and only for palladium(II) chloride was sulphur-donation considered probable. Their evidence was based on visible and infrared spectra, magnetic measurements, and arguments based on steric strain.

Interaction of a sulphoxide and a halide in an inert solvent, at low temperature, led to instant precipitation of the appropriate complex [1 : 1 in stoicheiometry for boron halides (F,Cl) and 2 : 1 for tin(IV) halides (Cl,Br,I)]. There were three exceptions to this behaviour [see (1)—(3)].

$$2Me_2SO + SiCl_4 \longrightarrow 2MeS{\cdot}CH_2Cl + SiO_2 + 2HCl \qquad \text{(1)}$$

$$\left.\begin{aligned} Me_2SO + BCl_3 &\longrightarrow MeS{\cdot}CH_2Cl + \tfrac{1}{3}(BOCl)_3 + HCl \\ MeS{\cdot}CH_2Cl + \tfrac{1}{3}(BOCl)_3 &\longrightarrow MeS{\cdot}CH_2Cl,BOCl \\ MeS{\cdot}CH_2Cl + BCl_3 &\longrightarrow MeS{\cdot}CH_2Cl,BCl_3 \end{aligned}\right\} \qquad \text{(2)}$$

$$2Ph_2SO + SiCl_4 \longrightarrow 2p\text{-}Cl{\cdot}C_6H_4{\cdot}SPh + SiO_2 + 2HCl \qquad \text{(3)}$$

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[1] Pickard and Kenyon, *J.*, 1907, **91**, 896.

[2] Hofman and Ott, *Ber.*, 1907, **40**, 4930.

[3] (*a*) Cotton and Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986; (*b*) Cotton, Francis, and Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534; (*c*) Horrocks and Cotton, *Spectrochim. Acta*, 1961, **17**, 134.

[4] (*a*) Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082; (*b*) Schläfer and Schaffernicht, *Angew. Chem.*, 1960, **72**, 618.

[5] Laughlin, *J. Org. Chem.*, 1960, **25**, 864.

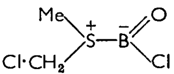
[6] (*a*) Gutmann and Utvary, *Monatsh.*, 1959, **90**, 706; (*b*) Gutmann, quoted in ref. 4*b*.

[7] Lindqvist and Zackrisson, *Acta Chem. Scand.*, 1960, **14**, 453.

The boron trichloride–dimethyl sulphoxide system has previously been examined by Cotton and Francis,[3a] and complex formation (Me_2SO,BCl_3, or more probably $Me_2SO,2BCl_3$) was then tentatively proposed. Our interpretation (reactions 2) rests on (i) analogy with reaction (1) and with thionyl chloride–sulphoxide reactions, and (ii) identification of the chloromethyl methyl sulphide complexes of boron oxychloride and trichloride. As to (i), Bordwell and Pitt [8] showed that thionyl chloride reacts with alkyl (or aryl) methyl sulphoxides to form hydrogen chloride, sulphur dioxide, and alkyl (or aryl) chloromethyl sulphides. As to (ii), the main non-volatile product of the boron trichloride–dimethyl sulphoxide reaction was the oxychloride complex (insoluble in methylene chloride), and a subsidiary one was the trichloride complex. The latter was also synthesised from the sulphide and boron trichloride. From either complex, the sulphide could be displaced by reaction with quinoline, confirming the structural assignments.

Sulphide complexes of boron trichloride are not new,[9] but the introduction of an α-chlorine atom might have been expected so seriously to weaken the donor strength of the sulphide as to prevent isolation of a complex (as it does in corresponding ethers [10]). In fact, the saturation vapour pressure of chloromethyl methyl sulphide–boron trichloride is 10 mm. at 20°.

The isolation of a boron oxychloride complex is interesting, since the free oxychloride is so unstable as to have had its existence questioned,[11] although spectroscopic evidence for its existence as a boroxole, $(ClBO)_3$, has now been obtained.[12] The only prior report of a boron oxychloride stabilised by co-ordination has been of the pyridine adduct.[13] The oxychloride–sulphide complex is thought to be more stable than the trichloride–sulphide complex, because (i) it is the major product of reactions (2), suggesting that, in the competition for sulphide, the oxychloride is the stronger acceptor, and (ii) the saturation vapour pressure of the oxychloride complex is negligible at room temperature. These observations are consistent with a monomeric structure (I) for the oxychloride complex, providing, so far as we are aware, a unique example of a co-ordination compound having a multiply bonded boron atom. Evidence for structure (I) also comes from the infrared spectrum, which shows strong (but broad) absorption at 1400—1450 cm.$^{-1}$, almost certainly due to the B–O stretching vibration.



(I)

The B–O stretching frequency in three-co-ordinate boron esters, $>$B–OR, falls at ~1350 cm.$^{-1}$, and in these compounds the B–O bonds already have appreciable double-bond character due to p_π–p_π-bonding.[14,15]

Reaction (3) has close analogy to early observations by Michaelis and his co-workers [16] on the behaviour of diphenyl sulphoxide with thionyl or phosphorus(V) chloride. Reaction (3) has been independently discovered by Issleib and Tzschach,[17] and is included in the present paper because of its relevance to the mechanism (4) proposed for sulphoxide–halide reactions, and because of the characterisation of the products.

It appears that, in general, the reaction of a sulphoxide and an electron-deficient metal or non-metal halide, MX-, proceeds by a nucleophilic attack of the former at M to produce a complex; unless the M–X bond is highly polarisable, in which case M–X heterolysis takes place (either synchronously or separately) and the next step is probably a 1 : 3 shift of halogen by an S_Ni mechanism (see reaction 4). The subsequent fate of the chlorosulphonium chloride is determined by the nature of the group R (alkyl or aryl).

That sulphoxides are strong donors was also shown by the formation of a stable complex

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[8] Bordwell and Pitt, *J. Amer. Chem. Soc.*, 1955, **77**, 572.

[9] Phillips, Hunter, and Sutton, *J.*, 1945, 146; Lappert, *J.*, 1953, 2784.

[10] Edwards, Gerrard, and Lappert, *J.*, 1957, 377.

[11] Martin, *Chem. Rev.*, 1944, **44**, 461.

[12] Goubeau and Keller, *Z. anorg. Chem.*, 1953, **272**, 203.

[13] Lappert, *J.*, 1953, 667.

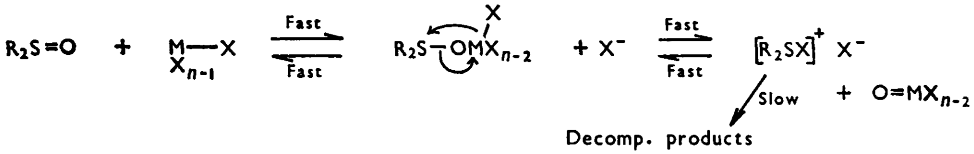
[14] Werner and O'Brien, *Austral. J. Chem.*, 1955, **8**, 355.

[15] Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2412.

[16] Michaelis and Godchoux, *Ber.*, 1891, **24**, 757; Loth and Michaelis, *Ber.*, 1894, **27**, 2540.

[17] Issleib and Tzschach, *Z. anorg. Chem.*, 1960, **305**, 198.

with tin(IV) iodide, which is normally a poor acceptor. On the other hand, dimethyl sulphoxide is evidently not as strong a base as pyridine, with respect to tin(IV) chloride as reference Lewis acid: it could not compete effectively with pyridine, when the chloride was added to a mixture of the two bases in methylene chloride [in which both the pyridine- and dimethyl sulphoxide–tin(IV) chloride complexes are insoluble].



. . . . . (4)

Infrared Spectra of the Sulphoxides and their Complexes, and the Structure of the Complexes.—The infrared spectra of a number of sulphoxides have been examined by Barnard, Fabian, and Koch,[18] and they established that the strong absorption band at ~1050 cm.$^{-1}$ arose from the S–O stretching vibration. The C–S stretching vibration in diphenyl sulphoxide was tentatively assigned [19] to a band at 684 cm.$^{-1}$. No attempt at a full co-ordinate treatment, with assignment of fundamentals, has yet been published even for the lowest homologue, dimethyl sulphoxide (although this is now in hand [3b, 3c]), and we therefore can do little else than describe the spectra of the sulphoxides and the changes that occur on complex-formation, in particular noting shifts in the S–O stretching frequency (Table 1). These results may be regarded as supplementary to recent reports by Cotton, Francis, and Horrocks [3b] on dimethyl sulphoxide complexes with cadmium, zinc, and tin(IV) chloride, cadmium bromide, and certain transition-metal derivatives.

TABLE 1. S–O *Stretching frequencies in sulphoxides and their complexes.*[a, b]

Compound	νS–O (cm.$^{-1}$) (mull [c])	νS–O (cm.$^{-1}$) (KBr disc)	$-\Delta\nu$[d] (cm.$^{-1}$)	Compound	νS–O (cm.$^{-1}$) (mull [c])	νS–O (cm.$^{-1}$) (KBr disc)	$-\Delta\nu$[d] (cm.$^{-1}$)
Me_2SO,BF_3	938	—	129	Pr^iBu^tSO,BCl_3	913	—	133
$(Me_2SO)_2,SnCl_4$	920, 905	919, 905	147, 162	Bu^t_2SO,BCl_3 ...	919	—	114
$(Me_2SO)_2,SnBr_4$	911, 903	913, 903	155, 164	Ph_2SO,BCl_3 ...	887	—	159
$(Me_2SO)_2,SnI_4$...	924, 904	920, 902	145, 164	$(Ph_2SO)_2,SnCl_4$	937, 913	937, 913	109, 133

[a] νS–O in (i) Me_2SO (2% solution in CCl_4) at 1067 cm.$^{-1}$, (ii) Pr^iBu^tSO (5% solution in CCl_4) at 1046 cm.$^{-1}$, (iii) Bu^t_2SO (6% solution in CCl_4) at 1033 cm.$^{-1}$, and (iv) Ph_2SO (5% solution in CCl_4) at 1046 cm.$^{-1}$. [b] The results are accurate to ±5 cm.$^{-1}$. [c] In liquid paraffin. [d] Average values.

With diphenyl sulphoxide, it is possible to go further because, with the very detailed discussion available of the various aromatic absorptions of the monohalogenobenzenes,[20] we can assign (Table 2) all the bands in the spectrum of diphenyl sulphoxide and of its complexes, with reasonable certainty. An interesting feature of these spectra is the splitting of the out-of-phase CH-aromatic deformation (B_2) into a doublet, with the two bands separated by about 20 cm.$^{-1}$. A similar observation [21] was made for spectra of compounds having two phenyl groups attached to a three-co-ordinate boron atom, $Ph_2B\cdot\ddot{Y}$ (Y = Hal, OR, OH, etc.), and for *NN*-diphenylacetamide and its boron trichloride complex.[22] On the other hand, such splitting is not invariably present in compounds having two phenyl groups joined to a common atom, *e.g.*, not in diphenylamine. It appears possible that the splitting arises from a coupling of modes caused by the close approach of the *ortho*-hydrogen atoms and this might be significant only when the common atom is multiply bonded to an adjacent one (as, *e.g.*, in $Ph_2\overset{-}{B}{=}\overset{+}{Y}$, Ph_2SO, etc.).

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[18] Barnard, Fabian, and Koch, *J.*, 1949, 2442.
[19] Cymerman and Willis, *J.*, 1951, 1332.
[20] Whiffen, *J.*, 1956, 1350.
[21] Abel, Gerrard, and Lappert, *J.*, 1957, 3833.
[22] Gerrard, Lappert, Pyszora, and Wallis, *J.*, 1960, 2144.

TABLE 2. *Diphenyl sulphoxide and its tin*(IV) *chloride complex; absorption bands* (*cm.*$^{-1}$) *and assignments.*

Ph$_2$SO ^{a}	(Ph$_2$SO)$_2$,SnCl$_4$ ^{b}	Assignment	Ph$_2$SO ^{a}	(Ph$_2$SO)$_2$,SnCl$_4$ ^{b}	Assignment
3053 (1) ^{c}	3053 (1) ^{d}	C–H stretch (A_1)	1155 (12)	1157 (13)	C–H deformn. (B_1)
1949 (2)	1980 (2)	Aromatic overtone and combination bands	1089 (13)	1078 (14)	Mass-dependent (A_1)
1876 (3)	1887 (3)		1071 (14)	1073 (15)	C–H deformn. (B_1)
1797 (4)	1818 (4)		1046 (15)	937 (18)	S–O stretch
1742 (5)	1795 (5)			913 (19)	
1580 (6)	1580 (6)	C–C stretch (A_1)	1020 (16)	1018 (16)	C–H deformn. (A_1)
		(masking B_1)	996 (17)	995 (17)	Ring deformn. (A_1)
1475 (7)	1473 (7)	C–C stretch (A_1)	911 (18)	913 (19)	C–H deformn. (B_1)
1443 (8)	1443 (8)	C–C stretch (B_1)			masked by νS–O
1321 (9)	1326 (9)	C–C stretch (B_1)	755 (19) ^{b}	763 (20)	C–H deformn. (B_2)
1302 (10)	1307 (10)	C–H deformn. (B_1)	735 (20) ^{b}	745 (21)	
	1290 (11)		692 (21) ^{b}	694 (22)	Ring deformn. (B_2)
1164 (11)	1173 (12)	C–H deformn. (A_1)	684 (22) ^{b}	679 (23)	C–S stretch

^{a} Solution (5%) in CCl$_4$. ^{b} KBr disc (A in Fig. 1). ^{c} Numbers in parentheses refer to location in Fig. 1. ^{d} Numbers in parentheses refer to location in Fig. 2.

The spectra of diphenyl sulphoxide (Fig. 1) and its tin(IV) chloride complex (Fig. 2) are reproduced and the location of absorption bands is indicated in Table 2, whilst the spectra of dimethyl, isopropyl-t-butyl, and di-t-butyl sulphoxide and some of their complexes are described in Table 5. It is clear that, on complex-formation, the only significant change in the diphenyl sulphoxide series is the large shift of the S–O stretching vibration to lower frequency. This is also evident with the aliphatic sulphoxides and their complexes, although further shifts are apparent in the 900—1150 cm.$^{-1}$ region. With the boron trichloride complexes, absorption bands due to B–Cl stretching vibration are readily distinguished (Table 3) [cf. CH$_3$·CO·NMe$_2$,BCl$_3$ (ref. 22) at 777, 753, and 713 cm.$^{-1}$; and RCN,BCl$_3$ (ref. 23) at 778, 733, and 711 cm.$^{-1}$], whilst the Sn–Hal stretching frequencies would not be expected to fall within the rock-salt region.

Infrared spectra of (FIG. 1) *diphenyl sulphoxide in carbon tetrachloride and* (A) *Nujol mull, and* (FIG. 2) *bis*(*diphenyl sulphoxide*)*tin*(IV) *chloride in a* KBr *disc.*

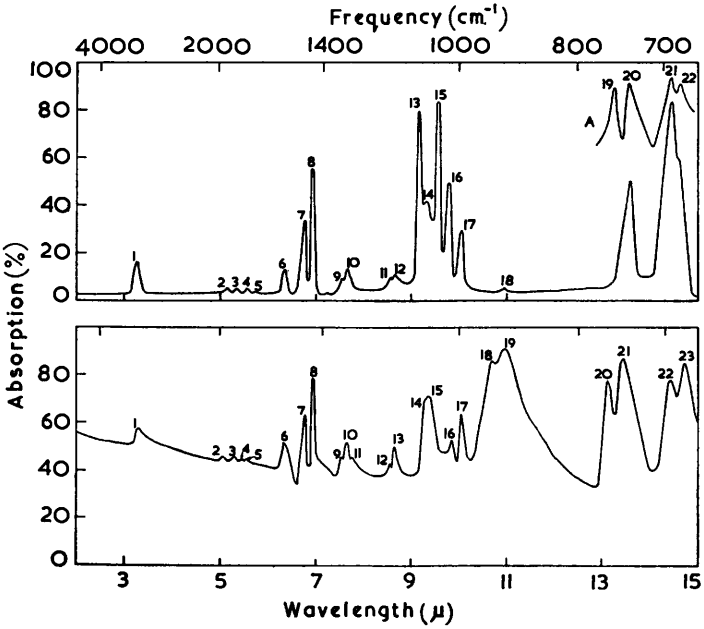

FIG. 1.

FIG. 2.

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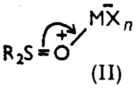
[23] Gerrard, Lappert, Pyszora, and Wallis, *J.*, 1960, 2182.

TABLE 3. B–Hal *Stretching frequencies in* R_2SO,BCl_3.

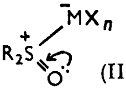
Compound	$Pr^iBu^tSO{\cdot}BCl_3$	Bu^t_2SO,BCl_3	Ph_2SO,BCl_3
νB–Cl	760, 714	767, 736	775, 723, 709

In the low-frequency region, absorption, probably due to the C–S stretching vibration, is also apparent in the aliphatic compounds [Me_2SO 686; Me_2SO,BF_3 685; $(Me_2SO)_2,SnCl_4$ 724; $(Me_2SO)_2,SnBr_4$ 724; $(Me_2SO)_2,SnI_4$ 719; Bu^t_2SO 682; Bu^t_2SO,BCl_3 671; and Pr^iBu^tSO,BCl_3 681 cm.$^{-1}$].

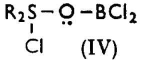
Possible structures for the sulphoxide complexes are (II) and (III); structure (IV) is



(II)



(III)



$R_2S(Cl)-\ddot{O}-BCl_2$ (IV)

only feasible for the boron trichloride adducts, because the B–Cl bond, unlike the other M–Hal bonds, is highly polarisable. It is relevant to consider structure (IV), because examples of boron trichloride addition to multiply bonded compounds are known (*e.g.*, for ketones [24] and certain olefins [25]).

The S–O bond in a sulphoxide may be regarded as substantially a double bond, with p_π–d_π ($\overset{-}{S} \longleftarrow \overset{+}{O}$) bonding from oxygen to sulphur superimposed on the SO σ-bond ($\overset{+}{S}$–$\overset{-}{O}$) (for bibliography, see ref.[3a]). Structure (II) for the complex implies a lengthening of the S–O bond (decrease in p_π–d_π bonding) in the complex compared with the free ligand and hence a decrease in the S–O stretching frequency would be expected; conversely, structure (III) requires an increase in S–O stretching frequency. This argument ignores (i) the mass effect of the acceptor, and (ii) the possibility of coupling between the SO and the MO oscillator. However, both these would cause an increase in the S–O stretching frequency and the experimentally observed substantial decreases (Table 2), therefore, unequivocally demonstrate that the oxygen is the donor atom in these sulphoxide co-ordination compounds. Structure (IV) may be discounted because the S–O single bond stretching vibration would then fall at much lower frequency than ~900 cm.$^{-1}$ and the B–Cl stretching vibration at much higher frequency [15,21] than ~700 cm.$^{-1}$.

It is noteworthy that the SO absorption is only split into a doublet in the spectra of those compounds in which there is a 2 : 1 ligand : acceptor ratio [this had not previously been noticed [3b] in the spectrum of $(Me_2SO)_2,SnCl_4$], and this might be taken as an indication that the ligands are placed *cis* to one another in the octahedral complexes. Thus, coupling between the two S–O vibrations through the metal (Sn) atom would give rise to symmetric and antisymmetric modes, and, whereas in a *trans*-complex the former mode would be infrared-degenerate, in a *cis*-complex they would both be infrared-active. However, as the spectral measurements were made on solid specimens (the complexes were insoluble in all the common non-polar organic solvents), other explanations are possible—particularly the non-equivalence of ligands in the crystal, whether in a *cis*- or a *trans*-complex.

EXPERIMENTAL

General Procedures.—The sulphoxides were purified by removal of water as the benzene azeotrope, followed by distillation, or by recrystallisation as appropriate. The halides were redistilled and recondensed (BCl_3) or recrystallised (SnI_4). Solvents were dried (P_2O_5) and redistilled. Halogen, boron, and tin (as appropriate) in complexes were estimated in an enclosed system, acidimetrically as hydrogen halide (Methyl Red) and boric acid (phenolphthalein in presence of mannitol) after hydrolysis with cold water; or as hydrogen halide (Volhard); or, for tin, by reduction with iron wire and hydrochloric acid and subsequent

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[24] Gerrard and Lappert, *Chem. Rev.*, 1958, **58**, 1081.

[25] Joy and Lappert, *Proc. Chem. Soc.*, 1960, 353.

iodometric determination in a nitrogen atmosphere. Pyridine was estimated by steam-distillation from potassium hydroxide and titration of the distillate with sulphuric acid (Bromophenol Blue). Microanalyses (C, H, and S) were carried out by Mr. V. Manohin and his staff, and we offer them our best thanks.

Infrared spectra were recorded with a Perkin–Elmer 21 spectrophotometer, with sodium chloride optics. Samples were studied as discs (KBr), mulls (liquid paraffin and hexachlorobutadiene), and solutions (CCl_4), as appropriate.

Precautions were taken during manipulative operations to avoid contamination by atmospheric moisture. M. p.s were taken in sealed capillary tubes.

Preparation of the Complexes.—These were obtained by dropwise addition of the sulphoxide in methylene chloride to the cooled (0°) halide (in appropriate stoicheiometry) in the same solvent; reactions were carried out on 0·01—0·1-molar scale and the total volume of solvent was 2—4 times the combined weights of reactants. Evolution of heat accompanied the formation of the white [or violet, in the case of the tin(IV) iodide] *complex*, which was filtered off, washed with methylene chloride, and freed from solvent at 20°/10 mm. The results are summarised in Table 4. Dimethyl sulphoxide–boron trifluoride [5] was characterised merely by its infrared spectrum and by its formation in quantitative yield.

TABLE 4.

	Yield		Found (%)				Required (%)			
Complex	(%)	M. p.*	C	H	Hal	M	C	H	Hal	M
$(Me_2SO)_2,SnCl_4$	97	270—300°	12·0	3·1	34·0	28·6	11·5	2·9	34·0	28·5
$(Me_2SO)_2,SnBr_4$	98	198—204	8·2	1·9	53·6	20·1	8·1	2·1	53·8	20·0
$(Me_2SO)_2,SnI_4$	100	167—168	6·3	1·4	65·2	15·4	6·1	1·5	64·9	15·2
Pr^iBu^tSO,BCl_3	75	†	33·3	6·4	37·4	3·8	31·7	6·1	40·0	4·1
$Bu^t{}_2SO,BCl_3$	92	†	32·9	6·2	36·0	3·7	34·4	6·5	38·1	3·9
Ph_2SO,BCl_3	100	†	47·1	3·9	32·5	3·4	45·1	3·2	33·3	3·4
$(Ph_2SO)_2,SnCl_4$	100	224—226	44·8	3·3	21·0	17·5	43·4	3·0	21·3	17·8

* These may be decomposition temperatures. † These did not become transparent, even at 300°.

Interaction of Silicon Tetrachloride and Diphenyl Sulphoxide.—Silicon tetrachloride (2·78 g., 1 mol.) in methylene chloride (10 ml.) was added to the sulphoxide (6·60 g., 2 mol.) in the same solvent (40 ml.) at 0°. There was a vigorous reaction. Hydrogen chloride was evolved and the white solid deposit of silica (0·98 g., 100%) ($\nu_{max.}$ 1149 and 1081 cm.$^{-1}$) was filtered off. Removal of solvent from the filtrate at 20°/10 mm. gave *p*-chlorophenyl phenyl sulphide (7·10 g., 99%). On distillation, this afforded the pure sulphide (4·30 g.), b. p. 154°/7 mm., n_D^{20} 1·6353. The infrared spectrum of this sulphide was very similar to that of diphenyl sulphide, except for a strong band at 817 cm.$^{-1}$ (C–Cl) and bands at 1946 and 1883 cm.$^{-1}$ (characteristic of a *para*-substituted phenyl group).

Interaction of Silicon Tetrachloride and Dimethyl Sulphoxide.—Dimethyl sulphoxide (15·4 g., 1 mol.) was added dropwise to silicon tetrachloride (33·5 g., 1 mol.) at 0°. Evolution of hydrogen chloride accompanied the exothermic reaction. Distillation of the mixture afforded chloromethyl methyl sulphide (14·6 g., 77%), b. p. 106—107°, n_D^{20} 1·4957 ($\nu_{max.}$ 1149 and 1081 cm.$^{-1}$), and a residue of silica (12·0 g., 100%).

Interaction of Boron Trichloride and Dimethyl Sulphoxide.—Dimethyl sulphoxide (3·1 g., 1 mol.) in methylene dichloride (10 ml.) was added dropwise (30 min.) to boron trichloride (4·65 g., 1 mol.) in the same solvent (10 ml.) at 0°. The reaction was highly exothermic. Hydrogen chloride was evolved (and was identified spectroscopically) and a white crystalline deposit of the complex, **boron oxychloride–chloromethyl methyl sulphide** (6·1 g., 97%) (Found: C, 16·5; H, 3·5; Cl, 43·6; S, 19·15; B, 6·5. $C_2H_5Cl_2OSB$ requires C, 15·12; H, 3·17; Cl, 44·65; S, 20·18; B, 6·8%), was formed, which was filtered off, washed with methylene dichloride (3 × 5 ml.), and freed from solvent at 20°/10 mm.

In other experiments, the yield of complex was less (~85%), and the filtrate, after removal of solvent, afforded the sulphide–trichloride complex, identified analytically and by comparing its infrared spectrum with that of the authentic sample.

In a further experiment, dimethyl sulphoxide (13·0 g., 1 mol.) in methylene dichloride (10 ml.) was added to boron trichloride (14·5 g., 1 mol.) in the same solvent (10 ml.) at 0°. The complex was not isolated, but to the reaction mixture at 0° quinoline (5 ml.) in methylene dichloride was added. Heat of reaction accompanied the liberation of chloromethyl methyl sulphide from its boron oxychloride complex. Fractional distillation gave the pure sulphide (2·6 g., 70%), b. p. 106—107°, n_D^{20} 1·4957.

Interaction of Boron Trichloride and Chloromethyl Methyl Sulphide.—Boron trichloride (4·1 g., 1·6 mol.) was added to chloromethyl methyl sulphide (2·1 g., 1 mol.) at −78°. The white crystalline complex, *boron trichloride–chloromethyl methyl sulphide* (4·5 g., 98%) (Found: Cl, 65·6; B, 5·0. $C_2H_5Cl_4SB$ requires Cl, 66·3; B, 5·06%), was isolated by removal of the excess of boron trichloride at −78°/5 mm. At room temperature and under a vacuum, the complex lost boron trichloride rapidly to give a yellow gum.

TABLE 5. *Principal absorption bands* (*max. in cm.*$^{-1}$) *in sulphoxides and complexes.*

Me_2SO [a]	$(Me_2SO)_2,SnCl_4$ [b]	Pr^iBu^tSO [c]	Pr^iBu^tSO,BCl_3 [d]	$Bu^t{}_2SO$ [e]	$Bu^t{}_2SO,BCl_3$
2994m	3003w	2963s	2924s [h]	2959vs	2972s [h]
2915m	2914w	2941m(sh)	2857s [h]	2915s(sh)	1477m(sh) [h]
1618w	1422m	2865m	1488m(sh) [h]	1466s	1464s [h]
1433vs	1408m	1471m(sh)	1473m(sh) [h]	1447s(sh)	1397m [h]
1412s	1395m	1458m	1460s [h]	1385m	1374s [h]
1401s	1323w	1383m(sh)	1443s(sh) [h]	1364vs	1220vw
1312s	1302w	1365m	1403m [h]	1279m	1190vw
1302s	1033m	1294w	1385m [h]	1223m	1155w
1145w	987m	1232w	1376m [h]	1217m	1078vw
1067vvs	947m(sh)	1175w	1372m(sh)	1166s	1029vw
1008s	919s	1155w	1235w	1099m	919s
942s	905s	1115w	1167m	1072m(sh)	820vw
917s	724w	1046s	1153m	1033vvs	800w
883m		1031m(sh)	1109vw	1018vs	767vw
686s		954vw	1052m	941w	736m
		935vw	1024w	931w	671m
		871vw	913vs	787w [g]	
		864vw	830w	682w	
		789vw [g]	810m		
			802m		
			763s(sh)		
			760s		
			714m		
			681s		

[a] 2% in CCl_4. [b] KBr disc. [c] 5% in CCl_4 and liquid paraffin mull (*g*). [d] Mulls in hexachlorobutadiene (*h*) and liquid paraffin. [e] 6% in CCl_4 and liquid paraffin mull (*g*). [f] Mulls in hexachlorobutadiene (*h*) and liquid paraffin.

Addition to the complex (4·5 g.) of quinoline (5 ml.) at 0°, and distillation afforded chloromethyl methyl sulphide (2·54 g., 62%), b. p. 106—107°, n_D^{20} 1·4957.

Addition of Tin(IV) *Chloride to a Mixture of Dimethyl Sulphoxide and Pyridine.*—The chloride (3·60 g., 1 mol.) in methylene chloride (10 ml.) was slowly added dropwise to a solution of the sulphoxide (5·00 g., 4·9 mol.) and pyridine (5·00 g., 4·6 mol.) in the same solvent (20 ml.) at 0°. Reaction was vigorous and the white solid tin(IV) chloride–dipyridine complex (5·60 g., 95%) (Found: Cl, 34·1; C_5H_5N, 35·7. Calc. for $C_{10}H_{10}Cl_4N_2Sn$: Cl, 34·0; C_5H_5N, 37·8%) was instantly precipitated, filtered off, washed with methylene chloride, and freed from solvent at 20°/10 mm. The identity of the complex was confirmed by comparison of its infrared spectrum with that of an authentic sample.

Infrared Spectra of the Complexes.—In Table 5 are shown the results necessary to supplement Table 2 and Figs. 1 and 2. The spectra of the four sulphoxides, and one complex for each, are either reproduced [Ph_2SO and $(Ph_2SO)_2,SnCl_4$] or described.

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