1098. *The Infrared Spectra of Some Addition Compounds of Aluminium and Gallium Trihalides*

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The infrared spectra of oxy-ether and thio-ether complexes with the chlorides and bromides of aluminium and gallium in the range 4000—265 cm.$^{-1}$ are reported and assignment of the frequencies is discussed.

There has recently been much interest in the infrared spectra of co-ordination compounds with regard to the assignment of metal–ligand stretching frequencies. This interest arises since direct information may be obtained about the nature of the co-ordinate bond from such measurements. These frequencies should, for the majority of ligand groups encountered, lie below 600 cm.$^{-1}$ and in the main, the region covered by cæsium bromide optics.

Many investigations have been made into the vibrational spectra of co-ordination complexes (by both infrared and Raman methods) including metal–carbon,[1–4] metal–nitrogen,[1,5,6] metal–phosphorus,[7,8] metal–oxygen,[1,9] and metal–halogen systems.[1,10–12] Little attempt has been made to study the spectra of metal–sulphur complexes although Fujita and Nakamoto[13] have analysed the spectrum of bis(dithio-oxalato)platinate(II), Coates and Parkin[8] report spectra of some alkyl-sulphide complexes of gold and palladium, and Livingstone[14] has studied some transition-metal complexes with various chelating sulphur ligands.

We have prepared a number of complexes of the type $MX_3{:}L$ where $M = Ga^{III}$ or Al^{III}, X = Br or Cl, L = an ether or sulphide grouping. These complexes contain M–X, M–S, and M–O bonds, and the assignment of the infrared frequencies corresponding to the associated vibrations should afford useful information about the co-ordinate bond, taken in conjunction with thermochemical and n.m.r. spectroscopic studies also being undertaken.[15] The complexes studied and the frequencies of the peaks obtained are summarised in Tables 1—5.

The Vibrational Model.—We may consider the complexes to be simple adducts of the respective ligand with the metal halide monomer. To support this, the conductivities of some related complexes are very low in the liquid state,[16] and the thio-ether complexes may be distilled *in vacuo* unchanged, the vapour pressures being somewhat higher than those of the parent acceptors. The possibility that some, if not all, of the complexes are dimeric cannot be excluded. Attempts to measure molecular weights in benzene and chloroform solutions proved unsuccessful.

In order to reach any reasonable interpretation of the infrared spectra, certain additional assumptions must be made about the molecules, in particular about the ways in which the various vibrations of the uncombined donors and acceptors may interact with

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TABLE 1

Infrared spectra of Me_2S and its molten complexes

Me_2S (l)	Me_2S (g)	$AlCl_3,Me_2S$	$GaCl_3,Me_2S$	$AlBr_3,Me_2S$	$GaBr_3,Me_2S$	Assignment
	2985s	3025m	3020m	3020m	3020m	ν CH
	2925s	2935mw	2932w	2932m	2930w	ν CH
	2863s	2830w	2830w	2830w	2824w	2δ C–H
1429vs	$\left.\begin{matrix}1440\\1425\\1420\end{matrix}\right\}$vs	1421s	1425s	1420s	1420s	δ C–H
		1360w	1350w	1349w	1342w	δ CH
				1332w		
1309s	$\left.\begin{matrix}1328\\1313\\1301\end{matrix}\right\}$s	1310w	1310w	1314w	1310w	δ CH
	1270vw	1267vw	1264vw	—	1270vw	CH_3 rock
1240sh	1240vw					
1028s	$\left.\begin{matrix}1034\\1018\end{matrix}\right\}$s	1038s	1040s	1039s	1038s	CH_3 rock
972s	970m	985s	992s	990s	990s	CH_3 rock
		960sh	960sh	965sh	965sh	
906 m	905vw	920vw	923w	920vw	930w	CH_3 rock
		802m	794w	780m	—	
741m	—	730m	725m	724w	721m	ν C–S(B_1)
691s	$\left.\begin{matrix}702\\691\end{matrix}\right\}$ms	680m	666m	666m	664m	ν C–S(A_1)
				490vw		
		580s	409s	444s	303s	M–X(E)
		500sh		408ms		
		408s	359ms	365ms		
286vw		328m	306m	308w		δ $C\widehat{S}C$

TABLE 2

Infrared spectra of Et_2S and its molten complexes

Et_2S	$AlCl_3,Et_2S$	$GaCl_3,Et_2S$	$AlBr_3,Et_2S$	$GaBr_3,Et_2S$
2970vs	2985m	2985ms	2980s	2985ms
2932vs	2946m	2945ms	2941s	2945ms
2880s	2882w	2883w	2882w	2885w
1442s	1448s	1449s	1443w	1446s
—	1421m	1420ms	1419m	1419ms
1379m	1394m	1388ms	1390m	1385ms
—	1293sh	1281m	1288sh	1280m
1260s	1270s	1265s	1263ms	1262s
1074ms	1082w	1079m	1079m	1079m
1047w	1051w	1051m	1051m	1050m
970m	975s	969s	969s	970s
—	800sh	816vw	820w	810vw
780mw	780m	780ms	778m	777ms
763m	—	—	—	—
736w	—	742vw	—	740mw
693mw	670m	665m	665m	665m
652w	629vw	620vw	625vw	625vw
635w	613vw	604vw	606vw	602vw
—	540s	402s	444s	302s
381vw	495m, sh	356ms	408m	
342vw	418ms		365mw	
		303m		
310vw	379m		308mw	
	328m, br			
	279m			

each other on complex formation. We have measured the spectra of the free donor molecules directly, but this cannot be done for the acceptors as they are normally dimeric. Therefore, we have used a simple model in an attempt to obtain the stretching vibrations of the free acceptors.

The acceptor molecules are assumed to be pyramidal, of C_{3v} symmetry. It has been found very convenient to assume a bond angle of 109° 28′, but this can be changed readily if circumstances require it. In these systems the central atom is never of much greater

TABLE 3

Infrared spectra of tetrahydrothiophen and its complexes (benzene solution)

THT (liq. film)	$AlCl_3$,THT	$GaCl_3$,THT	THT (liq. film)	$AlCl_3$,THT	$GaCl_3$,THT
		2970m	—	1076w	1082mw
2940vs	2940s	2950ms	957m	947m	950m
2862s	2870ms	2872m		908w	
1440ms	1436s	1439s	876m	876ms	878ms
	1426s	1428vs	816ms	806ms	805m
1310w	1310m	1313m	683m	* 657m	* 667m
	1275m	1278ms	520m	* 535s	* 402s
1257ms	1259s	1262s	470m	* 476sh	* 355s
1210vw	1210mw	1210mw	280vw		
1195mw	1200mw	1200sh		* 403ms	* 304m
1130w	1132mw	1134w		* 318m	

* Nujol mull.

TABLE 4

Infrared spectra of diethyl ether and its molten complexes

Et_2O	$AlCl_3$,Et_2O	$GaCl_2$,Et_2O	$AlBr_3$,Et_2O	$GaBr_3$,Et_2O
2990vs	2985s	2992s	2986s	2986s
2950s	2940w	2945m	2940w	2942w
		2915vw		2906w
2870vw	2887w	2882vw	2887w	2875vw
		1468m		1457m
1440m	1440s	1440m	1436s	1438m
1390s	1395s	1394s	1391s	1395s
1360m	1334m	1326w	1327m	1325w
	1285m	1290w	1285m	1288w
	1192s	1193m	1190s	1190m
1135vs	1146s	1150m	1142s	1147m
1070m	1091ms	1092m	1092ms	1089m
		1067mw		
1040w	1000vs	1005vs	990vw	1006vs
1022w	876s	883s	873s	885s
932mw				
909sh				
841mw	834m	830m	827m	826m
799w	790w	790m	790w	790w
500m	765s	765s	762s	760s
438ms	535s	510vw	546m	500vw
374m	408s	412s	446s	450vw
309w		361ms	406w	304s
			364m	

Briegleb and Lauppe report the following Raman lines (intensities in brackets) for $AlCl_3$,Et_2O; 2976 (10), 2901 (10), 1450 (5), 1262 (2), 1206 (1), 1054 (4), 891 (4), 823 (3), 690 (2), 625 (4), 534 (6), 406 (10), 310 (8).

TABLE 5

Infrared spectra of tetrahydrofuran and its complexes

THF *	$AlCl_3$,THF †	$GaCl_3$,THF †	THF *	$AlCl_3$,THF †	$GaCl_3$,THF †
	1305w	1300w		950ms	950m
1240vw	1254mw	1248w			910m
1185m	1176m	1172m		859sh	849sh
1070vs	1086m			832s	830s
	1042w	1035m	654s	530s	418s
	1041w			436ms	358ms
912vs	985s	990s			

* Liquid film. † Nujol mull.

mass than those around it and therefore the general distribution of vibrational frequencies will depend to a large degree on the relative masses concerned. For the purpose intended then, a simple valency force field will be sufficient. We make the further, probably rather crude, approximation that the stretching and bending vibrations of the molecule MX_3

are "separable." Under these conditions the stretching frequencies are given by the relationships:

$$2\pi c\nu\ (A_1) = [k(\mu_X + 1/3\mu_M)]^{\frac{1}{2}} \tag{1}$$

$$2\pi c\nu\ (E) = [k(\mu_X + 4/3\mu_M)]^{\frac{1}{2}} \tag{2}$$

where k is a force constant and μ_M and μ_X are the reciprocal masses of atoms M and X.

Consider now a molecule MX_3Y, where Y is attached to M on the three-fold axis such that the M–Y stretching force constant is k'. The two A_1 stretching modes are given by the secular determinant

$$\begin{bmatrix} k(\mu_X + 1/3\mu_M) - \lambda & -\ k\mu_M/\sqrt{3} \\ -k'\mu_M/\sqrt{3} & k'(\mu_Y + \mu_M) - \lambda \end{bmatrix} = 0$$

where

$$\lambda = 4\pi^2c^2\nu^2$$

and the E frequency by the same expression as before. Finally if we consider a tetrahedral molecule MX_4, by putting $k' = k$ and $\mu_Y = \mu_X$ we find that

$$2\pi c\nu\ (A_1) = (k\mu_X)^{\frac{1}{2}}$$

and

$$2\pi c\nu\ (T_2) = [k(\mu_X + 4/3\mu_M)]^{\frac{1}{2}}.$$

Thus, the E vibration is unaffected by the approach of Y in so far as the force constant k is not affected. There are two conclusions which we use in assignment of the frequencies in our complexes; first, that the E vibration will not change very much from complex to complex and secondly, that it should lie fairly close to the T_2 stretching frequency of the corresponding MX_4^- ion. We can also calculate the value of the A_1, M–X stretching, frequency for a given value of the E frequency. The frequency so obtained is an estimate of the value of the A_1 mode for the *free* acceptor and is only used as a rough guide in assigning the spectra of the combined molecules.

A survey of the spectra of the complexes and the free ligands indicate that the oxy-ether complexes can be treated as minor perturbations of the free ligand from 4000 cm.$^{-1}$ down to about 800 cm.$^{-1}$, whilst the thio-ethers can be so treated down to about 600 cm.$^{-1}$. These frequencies are not low enough to include the bending motions of the ligands. It is therefore necessary to make a brief survey of the low-frequency absorptions which might be anticipated.

For the low-frequency region we assume that the ligands behave as molecules LY_2 of C_{2v} symmetry, L being the donor atom. Y takes the place of the alkyl groups which are assumed to be rigid, at low frequencies. The complex, MX_3,LY_2, can have at most C_s symmetry; however, if a simple valency force field is used the situation does not become complicated. We make one major assumption, that the ligand molecule is so oriented that its two-fold axis coincides with three-fold axis of the acceptor; this is not in fact likely to be the case but it is doubtful whether this approximation will have any important effect on the following conclusions.

In developing the secular equations we have considered the following vibrations: M–X stretching, M–L stretching, L–Y stretching, and YLY bending. The M–X bending, MX, rocking, LY_2 rocking, and internal rotation have been considered to be of too low energy to contribute significantly to any vibrations above 250 cm.$^{-1}$. The secular determinant factorises in such a way that the vibrations which are unsymmetrical in the uncombined molecules (the acceptor E vibration and the ligand B_1) do not couple dynamically with each other or with any of the " symmetrical " vibrations. The " A " vibrations, *i.e.*, M–X, M–L, L–Y stretching, and YLY bending, clearly do couple, as can be deduced from their secular determinant shown in Table 6. As will be shown however, in most cases it is possible to separate out the symmetrical LY stretching mode.

The procedure adopted in attempting assignments is as follows:

1. The M–X stretching E mode is assigned by comparison with infrared and Raman data on the ion MX_4^- and by its consistency in a series of compounds.

2. The corresponding A_1 frequency is estimated, using equations 1 and 2.
3. The A_1 and B_1, LY stretching modes of the ligand are obtained from the literature where possible, otherwise it is generally found that they are the only two ligand frequencies which shift much on complex formation.
4. Where possible a ligand absorption is assigned to the YLY bending mode. In all cases where this has been done, the frequency was found to be near the region where the other A_1 vibrations might be expected, and strong coupling can be assumed to occur.
5. The possibility of metal–sulphur or metal–oxygen vibrations adding another A_1 mode in the cæsium bromide region is examined.

TABLE 6

Potential function: $2V = k_{\mathrm{MX}}\Sigma(\Delta r_{\mathrm{MX}})^2 + k_{\mathrm{ML}}(\Delta r_{\mathrm{ML}})^2 + k_{\mathrm{LY}}\Sigma(\Delta r_{\mathrm{LY}})^2 + k\delta(r_{\mathrm{LY}}\Delta\beta)$ where Δr_{MX}, Δr_{ML}, and Δr_{LY} are bond-length changes, and $\beta = \mathrm{L}\widehat{\mathrm{Y}}\mathrm{L} = \cos^{-1}(-1/4)$.

Secular equations:

$$A_1 \text{ modes} \quad \begin{vmatrix} k_{\mathrm{MX}}(\mu_{\mathrm{X}} + \frac{1}{3}\mu_{\mathrm{M}}) - \lambda & -k_{\mathrm{MX}}\mu_{\mathrm{M}}/\sqrt{3} & 0 & 0 \\ -k_{\mathrm{ML}}\mu_{\mathrm{M}}/\sqrt{3} & k_{\mathrm{ML}}(\mu_{\mathrm{M}} + \mu_{\mathrm{L}}) - \lambda & -k_{\mathrm{ML}}\mu_{\mathrm{L}}\frac{\sqrt{3}}{2} & k_{\mathrm{ML}}\mu_{\mathrm{L}}\sqrt{\frac{5}{2}} \\ 0 & -k_{\mathrm{LY}}\mu_{\mathrm{L}}\frac{\sqrt{3}}{2} & k_{\mathrm{LY}}(\mu_{\mathrm{Y}} + \frac{3}{4}\mu_{\mathrm{L}}) - \lambda & -k_{\mathrm{LY}}\mu_{\mathrm{L}}\sqrt{\frac{15}{8}} \\ 0 & k\delta\mu_{\mathrm{L}}\sqrt{\frac{5}{2}} & -k\delta\mu_{\mathrm{L}}\sqrt{\frac{15}{8}} & k\delta(2\mu_{\mathrm{Y}} + \frac{5}{2}\mu_{\mathrm{L}}) - \lambda \end{vmatrix} = 0$$

$$E \text{ mode: } k_{\mathrm{MX}}(\mu_{\mathrm{X}} + \tfrac{4}{3}\mu_{\mathrm{M}}) - \lambda = 0.$$

$$B_1 \text{ mode: } k_{\mathrm{LY}}(\mu_{\mathrm{Y}} + \tfrac{5}{4}\mu_{\mathrm{L}}) - \lambda = 0.$$

The Influence of Co-ordination of the Ligands.—When a ligand molecule co-ordinates to an acceptor, the vibrational spectrum of the ligand may be affected in several ways, two principal factors being involved. Dynamic coupling of the ligand–acceptor stretching vibration with ligand vibrations of the same symmetry species will in general raise the ligand frequencies. The addition of an extra bond to the donor atom may alter the internal force field of the ligand; in general the effect seems to be that frequencies are lowered, as a consequence of lower force constants, but this is not always the case.

The ligands used in this work may be described in terms of C_{2v} symmetry; the A_1 vibrations may be affected by dynamic coupling and the L–Y force constants should be the main ones affected by electronic changes. The details of each ligand are discussed separately.

Dimethyl sulphide. It may be seen from Table 1 that the spectra of the complexes are very similar to each other and to that of the free ligand. McCullough *et al.*[17] have assigned the ligand spectrum. Bands above 1300 cm.$^{-1}$ are due to the methyl groups and are hardly affected by complex formation. The methyl rocking vibrations, in the range 900—1300 cm.$^{-1}$, move to slightly higher frequencies; the shift is not likely to be due to dynamic coupling, but might be explained in terms of steric restriction of rocking vibrations in the complexes.

The two absorptions at 741 and 691 cm.$^{-1}$ of the (liquid) ligand are associated with B_1 and A_1 C–S stretching modes, respectively. They both move to lower frequencies in the complexes, the decrease being in the order $\mathrm{GaBr_3} > \mathrm{AlBr_3} > \mathrm{GaCl_3} > \mathrm{AlCl_3}$. The reverse order might be expected for the A_1 vibration from considerations of dynamic coupling with the metal–sulphur stretching vibration as the relevant off-diagonal terms are larger for aluminium than for gallium. As the difference between the A_1 and B_1 vibrations remains constant at about 50 cm.$^{-1}$, the decrease of the two is presumably due almost entirely to reduction of the C–S force constant in the complexes. It appears that the A_1 mode is, in all cases, sufficiently far removed from other A_1 vibrations for the dynamic coupling to be neglected.

The A_1 bending mode of dimethyl sulphide at 286 cm.$^{-1}$ is very likely to be in the same

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[17] J. P. McCullough, W. N. Hubbard, F. R. Frow, I. A. Hossenlopp, and G. Waddington, *J. Amer. Chem. Soc.*, 1957, **79**, 561.

region as other A_1 modes in the complexes and is therefore not considered in this section.

Diethyl sulphide. This is a more complicated molecule than dimethyl sulphide and band assignments are more difficult to make. However, at frequencies above 600 cm.$^{-1}$ the spectra of the complexes are very similar to that of the free ligand. The most noticeable changes are the small decreases of about 20 cm.$^{-1}$, in the frequencies of ligand bands at 693, 652, and 635 cm.$^{-1}$. The 693-cm.$^{-1}$ band increases in intensity on complex formation. By analogy with dimethyl sulphide, these bands may be associated with C–S stretching although the presence of three of them is difficult to explain. One possibility is a Fermi resonance between the A_1, C–S stretching mode and the first overtone of the C–S–C bending mode, or other low-frequency vibration. It is barely possible to separate the acceptor molecules in their relative effects on these three bands, although $AlCl_3$ has the smallest effect.

Diethyl sulphide shows three very weak absorptions between 300 and 400 cm.$^{-1}$, which may be ascribed to CSC and CCS deformation modes. They are so weak that it would not normally be expected they could be observed in the complex spectra under the conditions used. However it is possible that their intensities may be changed in the complexes; they do seem to appear in the spectrum of $AlCl_3,Et_2S$.

Tetrahydrothiophen (THT). The spectra of the two complexes were measured in benzene solution in the range 3000—700 cm.$^{-1}$ and as Nujol mulls below 700 cm.$^{-1}$, the free ligand as the pure liquid. Thus, the apparent differences between the spectra of the free ligand and of the complexes around 1030 cm.$^{-1}$ are probably due to masking of the complex spectra by the strong benzene absorption. Otherwise, the spectra are similar to each other down to 700 cm.$^{-1}$. The 683-cm.$^{-1}$ band of THT drops on co-ordination by 26 cm.$^{-1}$ for $GaCl_3$ and by 36 cm.$^{-1}$ for $AlCl_3$. This band is presumably associated with a ring-stretching mode involving movement of the sulphur atom; it is very strong in Raman emission.[18] The 520- and 470-cm.$^{-1}$ bands of the free ligand are not seen in the complex spectra.

Diethyl ether. The free ligand and the complexes have similar spectra from 4000 cm.$^{-1}$ down only to about 1300 cm.$^{-1}$. The complexes are similar to each other in the range 750—1300 cm.$^{-1}$ but considerably different from the free ligand. We assign the frequencies above 1300 cm.$^{-1}$ to various C–H modes and will not discuss them further.

The spectrum of ether in the region 700—1300 cm.$^{-1}$ is dominated by a very strong band at 1135 cm.$^{-1}$. Infrared and Raman studies of dimethyl ether [19] have led to assignments of bands at 920 and 1102 cm.$^{-1}$ to symmetrical A_1 and asymmetrical B_1 C–O stretching modes, respectively. In the boron trifluoride adduct [20] these bands are moved to 925 and 1020 cm.$^{-1}$. It is therefore feasible to assign the 1135-cm.$^{-1}$ band in diethyl ether to asymmetrical C–O stretching and to expect it to move to lower frequencies on co-ordination. This idea explains the considerable difference between the complexes and the free ligand, for it is likely that the fairly strong bands at 1145 and 1190 cm.$^{-1}$ in the complex spectra appear as the result of having been " unmasked " by movement of the much stronger C–O stretching frequency to about 1000 cm.$^{-1}$. We therefore assign the 1000-cm.$^{-1}$ band in the complexes as the B_1, C–O stretching mode and the band at about 880 cm.$^{-1}$, rather more tentatively, as its A_1 partner. Both of these bands occur in the order of increasing frequency $AlBr_3$, $AlCl_3$, $GaCl_3$, $GaBr_3$. This is a very different order from the one found for the corresponding bands in Me_2S complexes. Hamelin and Hayes [21] report the spectra of aluminium chloride and bromide in ether solutions over a limited frequency range; the chloride shows very good agreement with our results but the spectra of the bromide solution indicate that there may be differences between dilute solutions and the molten phase in this system.

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[18] H. Tschamler and H. Voetter, *Monatsh.*, 1952, **83**, 302.
[19] Y. Kanazaua and K. Nakada, *Bull. Chem. Soc. Japan*, 1962, **35**, 612.
[20] G. M. Begun, W. H. Fletcher, and A. A. Palko, *Spectrochim. Acta*, 1962, **18**, 655.
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The COC deformation of dimethyl ether is considered to occur at 420 cm.$^{-1}$, and at 499 cm.$^{-1}$ in the boron trifluoride complex.[20] The COC deformation of diethyl ether may be coupled with several vibrations such as CH_2 wagging, CCO deformation, etc., and the spectrum is more complicated than that of dimethyl ether, showing four bands at longer wavelengths. It is impossible to say whether any of these contain a large proportion of COC deformation in its normal co-ordinate, although it is reasonable to suppose that the band at 309 cm.$^{-1}$ contains very little.

The absorption at about 760 cm.$^{-1}$ by the complexes presents some difficulties. It is not present in the free ligand spectrum and is too high for any metal–halogen vibration. It is therefore very tempting to assign it to metal–oxygen stretching. However, it is unlikely that such a vibration would occur at virtually the same frequency for all four complexes, as changes of both metal and of halogen would be likely to affect it. It is also very probable that metal–oxygen stretching and COC deformation are strongly coupled in these complexes.

Briegleb and Lauppe [22] have measured the Raman spectrum of $AlCl_3,Et_2O$, but the agreement with our infrared data is very poor; intensities would not be expected to correspond, but all except A_2 fundamentals should occur in both types of spectrum. In particular, these workers report bands at 625 and 690 cm.$^{-1}$ (but nothing at 765 cm.$^{-1}$) which might be associated with COC deformation and metal–oxygen stretching.

Tetrahydrofuran (THF). The spectra of the complexes were measured as Nujols mulls and so no comparison with the free ligand is afforded above 1300 cm.$^{-1}$. One of the most striking features of the spectrum of THF is the complete absence of any definitive absorption below 650 cm.$^{-1}$, although the Raman spectrum [23] shows three low-frequency bands. However, the two strong bands at 1070 and 912 cm.$^{-1}$ are readily associated with two ring-stretching modes of species B_1 and A_1, respectively which involve stretching of CO bonds. On complexing, the B_1 moves to about 990 cm.$^{-1}$, but the position of the A_1 mode in the complexes is not definite. It is possible that frequencies at 950 and 830 cm.$^{-1}$ are both A_1 vibrations, consisting of ring stretching and ring deformation coupled together.

The Low-frequency Absorption Spectra.—Aluminium chloride complexes. All these complexes show strong absorption at about 540 cm.$^{-1}$ and in the range 400—420 cm.$^{-1}$, with the exception of the THF adduct which shows the second absorption at 436 cm.$^{-1}$. Comparable substances reported in the literature are $AlCl_4^-$, which shows the T_2 vibration [24] at 575 cm.$^{-1}$, $AlCl_3,SOCl_2$, $[(AlCl_3)_2SOCl_2]$,[25] $AlCl_3,NH_3$,[26] and $AlCl_3,Et_2O$,[22] which all show Raman bands at 540 ± 10 cm.$^{-1}$. We therefore assign the 540-cm.$^{-1}$ band in these complexes as the degenerate Al–Cl stretching vibration. Calculation from the mass ratio indicates that the corresponding A_1 vibration would lie at about 390 cm.$^{-1}$, or somewhat higher if the bond angle Cl–Al–Cl were less than 109° 28′. It seems , therefore, to be very reasonable to assign provisionally the absorptions at about 410 cm.$^{-1}$ to this A_1 stretching mode.

Sulphide complexes. In the case of dimethyl sulphide, it has been shown that the symmetrical C–S stretching mode at about 670 cm.$^{-1}$ probably does not couple very strongly with the other lower-energy A_1 modes, and so it might be anticipated that the three modes, Al–Cl stretching, Al–S stretching, and C–S–C deformation, will form a group coupled together. There appear to be two ways of interpreting the data.

The three complexes each show three absorptions at frequencies lower than the E absorption, a shoulder at about 500 cm.$^{-1}$, and peaks at about 410 and 305 cm.$^{-1}$. We have already provisionally assigned the 410-cm.$^{-1}$ peak to symmetrical Al–Cl stretching. We may consider two alternative assignments in the system.

(A) Since the symmetry of the molecule is not strictly C_{3v}, but at most C_s, there

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[26] J. Goubeau and H. Siebert, *Z. anorg. Chem.*, 1947, **254**, 126.

should be no degeneracies. It is therefore possible that the two components of asymmetrical Al–Cl stretching have observably different frequencies. This situation may arise if the alkyl groups of the ligands interacted sterically with the chlorine atoms, *i.e.*, if rotation about the Al–S bond were severely restricted. In this case the 500-cm.$^{-1}$ bands would be assigned as Al–Cl stretching. The peak at 305 cm.$^{-1}$ remains as due to either Al–S stretching or to ligand deformation. It is more intense than the deformation mode in the free ligand; such a mode could be made more intense by resonance with Al–S stretching, and with the Al–Cl stretching vibration at 410 cm.$^{-1}$. If this assignment were correct, we must then assume that the Al–S stretching frequency lies below 265 cm.$^{-1}$. Otherwise the Al–S stretching would be at 305 cm.$^{-1}$.

(B) If we assume that the degeneracy of the unsymmetrical Al–Cl stretching vibration is not removed, then the three bands observed below the E mode can readily be assigned to the three A_1 modes expected. It is probable that they would be strongly coupled to each other, but in this case it is possible to reach some conclusions about which particular bond predominates in the normal co-ordinate corresponding to each frequency. As already indicated, the bond near 410 cm.$^{-1}$ is remarkably close to the value calculated for the Al–Cl stretching mode A_1, and therefore consists primarily of this mode. The 305-cm.$^{-1}$ bond may very readily be associated with ligand bending, having a higher frequency than the free ligand because of steric restriction on this motion. By elimination, the 500-cm.$^{-1}$ bond is largely due to Al–S stretching.

We think that assignment (B) is the more likely to be correct for the following reasons. (i) Shoulders on the E vibration are shown only by the thioether–aluminium chloride complexes. If they were due to removal of the degeneracy by steric effects then the splitting should be shown more strongly by oxy-ether compounds, as indicated by models, whereas no such splitting is observed with oxy-ethers. Furthermore, models show that tetrahydrothiophen and dimethyl sulphide are remarkably free from steric interactions of this type when co-ordinated to a metal. (ii) In the skeleton ($SAlCl_3$), aluminium is the lightest atom, and sulphur and chlorine have quite similar masses. It might therefore be expected that these complexes should be dynamically rather similar to the tetrahedral species $AlCl_4^-$, and so could be treated as being tetrahedral with a perturbation of C_{3v} symmetry. The T_2 mode of the tetrahedral system would split into E and A_1 modes. The tetrahedral A_1 mode would remain as A_1, but would have a much lower frequency. (iii) In assignment (A), if the 305-cm.$^{-1}$ band is taken as Al–S stretching, then the situation arises where the ligand deformation does not appear. It could not be masked by Al–S stretching as it has the same symmetry. It would be unlikely that the ligand deformation should move to lower frequencies on co-ordination. (iv) Similarly if the 305-cm.$^{-1}$ band is taken to be the ligand deformation, then the Al–S stretch must be below 265 cm.$^{-1}$. This would imply a force constant below 0·7 md/Å which seems to us to be unlikely for two light elements. (v) The spectrum of $AlCl_3,(Me_2S)_2$ is very similar but for a marked intensification of absorption at 500 cm.$^{-1}$.

Oxy-ether complexes. As has already been shown, the ligand spectra here are very different in the complexes from the free state. We assign the two low-frequency bands, 535 and 408 cm.$^{-1}$ in the ether complex (538 cm.$^{-1}$ intensity 10, and 406 cm.$^{-1}$ intensity 6, in the Raman spectrum),[22] 530 and 436 cm.$^{-1}$ in the THF complex, to the E and A_1, Al–Cl stretching modes, respectively.

It is, however, very difficult to determine the positions of the aluminium–oxygen and ligand deformation modes. A number of workers [9,27–31] have assigned various aluminium–oxygen frequencies in the range 400—700 cm.$^{-1}$. In the ether complex, it is possible

[27] E. R. Lippincott, J. A. Psellos, and M. C. Tobin, *J. Chem. Phys.*, 1952, **20**, 536.
[28] J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, 1962, **36**, 324, 331.
[29] Y. Kakinti, S. Kida, and J. V. Quagliano, *Spectrochim. Acta*, 1963, **19**, 201.
[30] R. E. Hester and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 513.
[31] C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, *J.*, 1961, 2601.

that one of these vibrations is masked by the E absorption and that the other corresponds to the strong band at 765 cm.$^{-1}$. It is very tempting to assign the latter to metal-oxygen stretching as it is absent from the free ligand spectrum. However, the complete absence of any comparable absorption in the THF complex would count very strongly against such an assignment. There is the possibility that THF acts as a rigid molecule up to 830 cm.$^{-1}$, with an effective mass of 72 and a consequent drop in the " metal-oxygen " frequency to a value well below 300 cm.$^{-1}$.

Briegleb and Lauppe[22] report a strong Raman band in $AlCl_3,Et_2O$ at 310 cm.$^{-1}$. There is no sign of this frequency in the infrared spectrum and we have found no suitable explanation for this.

Gallium chloride. All the complexes show a strong band between 400 and 420 cm.$^{-1}$, comparing with the T_2 vibration[32] of $GaCl_4^-$ at 386 cm.$^{-1}$. This band is assigned to the E vibration. Calculation gives the A_1 vibration at about 350 cm.$^{-1}$, compared with bands at 361 (diethyl ether) and 358 cm.$^{-1}$ (THF).

Sulphur complexes. The three complexes absorb strongly at 355—360 cm.$^{-1}$ and also at about 305 cm.$^{-1}$. Apparently one A_1 mode has not been observed and there are three possible explanations: (i) that the expected absorption is vanishingly weak; (ii) that the frequency is below 265 cm.$^{-1}$ and thus beyond the range of our instrument; (iii) that it is masked by the very strong E absorption.

Explanation (iii) seems the most likely from comparison with the aluminium complexes. The observed bands are assigned as Ga–Cl sym. stretching (355 cm.$^{-1}$) and CSC bending (305 cm.$^{-1}$) from arguments similar to those used for aluminium chloride complexes. The band at 305 cm.$^{-1}$ is much more intense in these complexes than in the $AlCl_3$ case. This is entirely consistent with coupling between the A_1 M–S stretching, M–Cl stretching, and ligand deformation modes, for the three are much closer together in $GaCl_3$ complexes than they are in $AlCl_3$ complexes.

Oxy-ether complexes. In the ether and THF complexes the E and A_1 Ga–Cl stretching modes are observed at about 415 and 360 cm.$^{-1}$, respectively. The situation with respect to metal-oxygen and ligand deformation modes is the same as with $AlCl_3$. Various gallium-oxygen frequencies have been assigned[9,30] in the range 400—600 cm.$^{-1}$.

Aluminium bromide complexes. All these complexes show strong absorption at 445 cm.$^{-1}$. The spectrum of $AlBr_4^-$ does not appear to have been measured, but the complex of $AlBr_3$ with methyl bromide[24] shows a broad depolarised Raman line at 452 cm.$^{-1}$ and the ethyl bromide complex a line at 449 cm.$^{-1}$. These lines have been assigned by Rice and Bald to asymmetrical Al–Br stretching modes, and so we assign the 445 cm.$^{-1}$ in the ether complexes in the same way.

Calculation gives the corresponding A_1 mode at 280 cm.$^{-1}$. Methyl bromide-aluminium bromide shows polarised Raman lines at 194 and 271 cm.$^{-1}$ (the ethyl complex[33] is very similar but no polarisation data are available), which have been assigned to A_1 vibrations of terminal Al–Br stretching and stretching of the Al–Br(Me) system, respectively. The appearance of the Me_2S and Et_2S spectra are not alike at long wavelengths, for although the frequencies are very similar, relative intensities are quite different. The Et_2S complex shows the E vibration at 444 cm.$^{-1}$ and four other bands below 500 cm.$^{-1}$. It seems probable that one of the ligand deformations borrows intensity from other vibrations, the most likely candidates being the relatively weak bands at 365 and 408 cm.$^{-1}$. It would be very reasonable to assign the fairly strong absorption at 308 cm.$^{-1}$ to the A_1, Al–Br stretch, but it is totally absent from the Et_2O complex and only very weak absorption appears there in the Me_2S complex. In the latter compound, the strong absorption is at 365 cm.$^{-1}$. It is possible that this could be the A_1, Al–Br stretch, but if so equations 1 and 2 must be modified to allow an angle of less than 100°.

Both the sulphide complexes show a weak band at 490 cm.$^{-1}$. We think that this may

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[32] L. A. Woodward and A. A. Nord, *J.*, 1956, 3721.

[33] B. Rice and K. C. Bald, *Spectrochim. Acta*, 1964, **20**, 721.

be associated with metal–sulphur stretching, but its weakness must count against such an assignment.

The band at 408 cm.$^{-1}$ is of doubtful existence in the Me_2S complex, but quite prominent in the Et_2S derivative. There is also a weak band at 402 cm.$^{-1}$ in the Et_2O complex. It is possibly due to ligand deformations in the ethyl compounds.

$AlBr_3,Et_2O$ shows a fairly sharp band at 546 cm.$^{-1}$ which is unique among these complexes. It is quite probably to be associated with aluminium–oxygen stretching and ligand COC bending, but the absence of any comparable band in other compounds is surprising.

Gallium bromide complexes. These substances each show strong absorption near 300 cm.$^{-1}$ which can therefore be assigned as the E vibration. It compares with 278 cm.$^{-1}$ found for the T_2 vibration [34] of $GaBr_4^-$. The calculated value of the corresponding A_1 vibration is 224 cm.$^{-1}$ which is clearly below the cæsium bromide region. It is, however, disappointing that in none of the spectra are other bands seen which might be associated with metal–oxygen or metal–sulphur stretching vibrations.

The data reported here offer a good basis for discussion of effects on the ligands due to co-ordination, and in all cases it has been possible to assign the unsymmetrical metal–halogen stretching frequency.

Effects on the ligands are very marked with respect to the C–O stretching vibrations in the ethers, but not so strong in the case of the thio-ethers.

The Al–Cl, E frequency is lower in these complexes than the comparable T_2 frequency [24] of $AlCl_4^-$. The factors involved in the decrease are likely to be a lowering of the stretching force constant and possibly a decrease of the Cl–Al–Cl angle. The reverse is noted in the cases of $GaCl_3$ and $GaBr_3$ complexes, when they are compared with $GaCl_4^-$ and $GaBr_4^-$.

The position with regard to the A_1 vibrations is not satisfactory. In the chloride complexes reasonable assignments have been obtained, but it is clear that no frequency can *a priori* be assigned to a particular bond stretching or angle deformation mode. Raman data would be very useful in confirming some of the assignments, and in order to elucidate the details of the vibrations, a co-ordinate analysis is required. In the cases of the bromides, coupling of various modes seems to be considerable and it is certain that our data are not complete, as spectra at wavelengths greater than 38 μ are clearly necessary.

EXPERIMENTAL

Preparation of Halides.—The metal halides were prepared by direct combination of the elements and purified by six successive sublimations *in vacuo*.

Purification of Ligands.—The commercial materials were purified by repeated fractional distillation from sodium, the middle fraction being taken in each case.

Preparation of Complexes.—The 1 : 1 addition compounds of aluminium and gallium trichlorides with dimethyl sulphide, diethyl sulphide, tetrahydrothiophen, and tetrahydrofuran have been characterised by m. p.–composition diagrams and were prepared in the present study by distilling the stoicheiometric quantity of the ligand on to the metal halide using standard vacuum techniques. The previously reported complexes $AlCl_3{\cdot}EtO$,[35] $AlBr_3{\cdot}Et_2O$,[36] $GaCl_3{\cdot}Et_2O$,[37] and $AlBr_3{\cdot}Me_2S$ [38] were prepared in a similar manner. The remaining complexes were prepared by distillation *in vacuo* of an excess of ligand on to the metal halide, and equilibration of the mixture followed by removal of excess of ligand under vacuum.

The products were analysed using standard techniques and the results are as follows:

$AlBr_3{\cdot}Et_2S$, m. p. $-3°$ (Found: C, 13·22; H, 2·77; S, 8·85; Br, 67·34. $C_4H_{10}AlBr_3S$ requires C, 13·54; H, 2·83; S, 8·95; Br, 67·2%).

$GaBr_3{\cdot}Me_2S$, m. p. 17·5° (Found: C, 6·45; H, 1·60; Br, 64·20. $C_2H_6Br_3GaS$ requires C, 6·46; H, 1·62; Br, 64·60%).

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[34] L. A. Woodward and A. A. Nord, *J.*, **1955**, 2655.

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[36] W. Menzel and M. Fröhlich, *Ber.*, 1942, **75**, *B*, 1055.

[37] N. N. Greenwood and P. G. Perkins, *Pure Appl. Chem.*, 1961, 255.

[38] H. Bohme and E. Boll, *Z. anorg. Chem.*, 1957, **290**, 17.

$GaBr_3$·Et_2S, m. p. 6·8° (Found: C, 12·12; H, 2·53; S, 8·23; Br, 59·93. $C_4H_{10}Br_3GaS$ requires C, 12·02; H, 2·50; S, 8·00; Br, 60·00%).

$GaBr_3Et_2O$, m. p. 23·0° (Found: C, 12·7; H, 2·60; Br, 61·31. $C_4H_{10}Br_3GaO$ requires C, 12·52; H, 2·62; Br, 62·55%).

Determination of Infrared Spectra.—All the spectra were obtained on a Perkin-Elmer 221 instrument equipped with grating and rock salt and cæsium bromide optics, and such sample was run at least twice.

Spectra in the sodium chloride region were obtained either as thin liquid films (in the case of the low-melting complexes), or as Nujol mulls, between sodium chloride plates. The samples were prepared in a nitrogen-filled glove box and the edges of the plates sealed round with Apiezon sealing compound.

For spectra in the cæsium bromide region, the thin liquid films or mulls were supported between two sheets of 1/10 mm. thick polyethylene clamped in a hollow to give an air-tight seal. The polyethylene was transparent in the region 700—250 cm.$^{-1}$ as also was the Nujol used in these experiments. During operation in the cæsium bromide region the instrument was flushed with dry nitrogen.

Et_2S was also measured between two CsBr pressed discs.

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