433. *Spectra and Structure of Amide Complexes.*

By W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis.

The infrared spectra of eleven amide complexes with boron halides (Cl, Br) and titanium tetrachloride have been measured. The virtual absence of hydrogen-bonding in primary and secondary amide complexes and the observation of frequency shifts (of ν_{NH}, amide I, II, III, and V bands, δ_{CH}, and ν_{BX}) relative to free amides and boron halides (also in tertiary amide complexes) are consistent with donation by oxygen and not by nitrogen. The same conclusion is derived from the nuclear magnetic resonance spectrum of *NN*-dimethylformamide–boron trichloride, which shows a chemical shift between the two sets of protons of the NMe_2 group and spin-spin coupling with the aldehydic hydrogen. Stereochemical questions are discussed.

In an earlier paper,[1] the preparation and reactions of some amide–boron trihalide (Cl, Br) complexes and of the titanium tetrachloride–*N*-methylacetamide complex were described. We now report their infrared spectra and nuclear magnetic resonance spectra, the latter for two complexes only. The object of this work was essentially to establish the structures, but other features considered are (1) the nature of changes in bond strengths in the amide molecule on co-ordination, (2) stereochemical aspects, and (3) comparison of the two (BCl_3 and BBr_3) systems.

The structure of primary and secondary amides themselves has been much discussed, particularly in terms of the relative importance of amido- and imido-forms. It is now realised that in general the tautomerism lies almost completely on the side of the amido-structure.[2] Amides form salts, *e.g.*, hydrochlorides, and act as ligands to electron-deficient molecules (for bibliography, see ref. 1). By analogy with amines it has frequently been assumed (see, *e.g.*, ref. 3) that the structure of the amide hydrochlorides involves protonation of the nitrogen atom, and many physicochemical data [4] have been brought forward in support of this. On the other hand, evidence [5,6] increasingly suggests that the hydrochlorides are oxonium salts. In only one work on amide complexes with electron-deficient molecules, the cadmium chloride complex of *N*-methylacetamide,[7] has evidence (infrared spectroscopy) been presented in favour of a definite structure; this was for nitrogen donation, but we shall here show that the data are consistent with our own view of oxygen donation.

Structures that require consideration are (I), (II), and (III) (we show a secondary amide with a boron halide as the acceptor molecule).

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[1] Gerrard, Lappert, and Wallis, preceding paper.

[2] Wheland, " Resonance in Organic Chemistry," Wiley, New York, 1956, p. 410; Bates and Hobbs, *J. Amer. Chem. Soc.*, 1951, **73**, 2151; Worsham and Hobbs, *ibid.*, 1954, **76**, 206; Kotera, Shibata, and Son, *ibid.*, 1955, **77**, 6183.

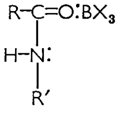
[3] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 786.

[4] Spinner, *Spectrochim. Acta*, 1959, 95.

[5] Fraenkel and Niemann, *Proc. Nat. Acad. Sci. U.S.A.*, 1958, **44**, 688.

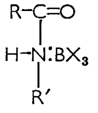
[6] Hantzsch, *Ber.*, 1931, **64**, 661; Huisgen and Brade, *Ber.*, 1957, **90**, 1432.

[7] Martinette, Mizushima, and Quagliano, *Spectrochim. Acta*, 1959, 77.



$R{-}C(=O{:}BX_3){-}N(H){:}{-}R'$

(I)



$R{-}C(=O){-}N(H)({:}BX_3){-}R'$

(II)

$[R\cdot CO]^+[R'\cdot NH,BX_3]^-$

(III)

Infrared Spectra.—(i) *Association in complexes.* The infrared spectra of amides are difficult to interpret, as many of the absorptions are not localised within particular atomic pairs. In the main, we shall discuss the so-called amide I, II, and III bands and the NH stretching frequencies in primary ($R\cdot CO\cdot NH_2$) and secondary ($R\cdot CO\cdot NHR'$) amides

TABLE 1.

Compound	Free amide dil. soln. (CH_2Cl_2)	Free amide liquid (or paraffin mull)	BCl_3 Complex dil. soln. (CH_2Cl_2)	BCl_3 Complex paraffin mull	BBr_3 Complex dil. soln. (CH_2Cl_2)	BBr_3 Complex paraffin mull
(*a*) NH *Stretching frequencies* (*cm.*$^{-1}$) *of amides and their complexes.*[1]						
$CH_3\cdot CO\cdot NH_2$	3559	3333	3448	3436	3448	3436
	3436	3175	3367	3367	3367	3356
			3289	3289	3279	3279
$Ph\cdot CO\cdot NH_2$	3553	3367	3448	3444		
	3436	3145	3333	3336		
			3247	3268		
$CH_3\cdot CO\cdot NHMe$ [2]	3460	3300	3367	3367		3289
$CH_3\cdot CO\cdot NHPh$	3425	3311	3367	3378		
	3289	3145	3279	3289		
$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$-*p*	3472	3263	3289			
(*b*) *The amide I band* (*cm.*$^{-1}$) *in amides and complexes.*[3]						
$CH_3\cdot CO\cdot NH_2$	1685	1685	1661	1658	1658	1658
$Ph\cdot CO\cdot NH_2$	1678	1658	1647	1658		
$CH_3\cdot CO\cdot NHMe$ [4]	1669	1653	1650	1661	1645	1654
$CH_3\cdot CO\cdot NHPh$	1684	1631	1626	1647		
$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$-*p*	1689	1647	1623	1645		
$H\cdot CO\cdot NMe_2$ [5]	1675	1661 [6]	1686	1692		
$CH_3\cdot CO\cdot NMe_2$	1634	1634	1633	1645	1635	1642
$CH_3\cdot CO\cdot NPh_2$	1661	1664	1553	1553		
(*c*) *The amide II band* (*cm.*$^{-1}$) *in amides and complexes.*[7]						
$CH_3\cdot CO\cdot NH_2$	1595	1626	1550	1548	1546	1541
$CH_3\cdot CO\cdot NHMe$ [8]	1528	1567	1538	1536	1536	1527
$CH_3\cdot CO\cdot NHPh$	1524	1558	1553	1553		
$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$-*p*	1515 [9]	1560	1550	1548		
(*d*) *The amide III band* (*cm.*$^{-1}$) *in amides and complexes.*[10]						
$CH_3\cdot CO\cdot NHMe$ [11]	1266	1299	1323	1332	1323	1325
$CH_3\cdot CO\cdot NHPh$	1312	1326	1370	1370		
(*e*) *The* CH (*in* Me·N<) *deformation mode* (*cm.*$^{-1}$).[12]						
$CH_3\cdot CO\cdot NHMe$ [13]	1412	1413	1408	1408	1406	1408
$CH_3\cdot CO\cdot NMe_2$	1401	1399	1401	1397	1399	1390

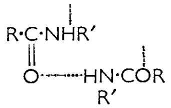
References in the body of this table are numbered independently of those in the main text and refer to the footnotes in Table 1.

[1] These results show deviations of ±10 cm.$^{-1}$. [2] The free amide in the vapour has ν_{NH} at 3500 cm.$^{-1}$; the cadmium chloride complex (potassium bromide disc) at 3400 cm.$^{-1}$;[7] and the titanium tetrachloride complex (paraffin mull) at 3289 cm.$^{-1}$. [3] The results show deviations of ±5 cm.$^{-1}$. [4] The free amide in the vapour has Amide I band at 1718 cm.$^{-1}$; the titanium tetrachloride complex (in CH_2Cl_2) at 1654 cm.$^{-1}$; and the cadmium chloride one (KBr disc) at 1650 cm.$^{-1}$ (ref. 7). [5] The boron trifluoride complex at 1695 cm.$^{-1}$ (ref. 12). [6] Broad. [7] These results show deviations of ±5 cm.$^{-1}$. [8] The free amide in the vapour has Amide II at 1487 cm.$^{-1}$; the titanium tetrachloride complex (in CH_2Cl_2) at 1530 cm.$^{-1}$; and the cadmium chloride complex (KBr disc) at 1555 cm.$^{-1}$ (ref. 7). [9] Overlapping with aromatic C=C stretching mode. [10] These results show deviations of ±3 cm.$^{-1}$. [11] The free amide in the vapour has Amide III at 1247 cm.$^{-1}$; the titanium tetrachloride complex at 1310 cm.$^{-1}$; and the cadmium chloride complex (KBr disc) at 1300 cm.$^{-1}$ (ref. 7). [12] These results show deviations of ±3 cm.$^{-1}$. [13] The titanium tetrachloride complex has the band at 1403 cm.$^{-1}$; the cadmium chloride complex at 1418 cm.$^{-1}$ (ref. 7).

and their complexes; the tertiary amides ($R{\cdot}CO{\cdot}NR'_2$) and complexes are discussed separately, and other assignments considered for all classes are certain CH deformation frequencies and absorptions due to the B–X stretching mode. A complete theoretical treatment of the *N*-methylacetamide molecule has recently been made,[8] and we rely on this in our discussion of amide I—V bands, generally. However, no such treatment appears to be available on tertiary amides, and this has necessitated our making tentative assignments (see Table 2) for certain absorption bands.

The amide I band arises almost exclusively ($>80\%$) from the carbonyl stretching mode, the amide II band has contributions from the NH in-plane bending ($\sim60\%$) and CN stretching modes, the amide III band arises from the CN stretching ($\sim40\%$), NH in-plane bending ($\sim30\%$), and the CH [of group R in (I)—(III)] deformation modes, and the amide V band represents the NH out-of-plane bending mode.

The infrared spectra of all the complexes have been measured both as mulls in liquid paraffin and as dilute solutions in methylene chloride, and there were no significant differences. On the other hand, with free amides, large frequency shifts in absorptions associated with NH and CO bonds occur under these conditions (and still further changes take place when spectra are examined in the vapour state). These shifts in free primary and secondary amides have been explained in terms of intermolecular hydrogen-bonding (IV),[9] which is dependent on the degree of molecular aggregation. The absence of comparable shifts in complexes shows that these are not (or, if so, only weakly) associated and this is consistent with structure (I), but not with (II). Thus, whilst in (I) the carbonyl-oxygen atom would no longer be nucleophilic, the tendency for hydrogen-bonding in (II) would be expected to be greater (except for steric effects) even than in the free amide because of the positive charge on the nitrogen atom to which the hydrogen is attached. With regard to comparison of particular absorption bands as between their positions in the free amides and their complexes, it is clearly necessary that both be considered in unassociated forms. Thus the reference spectra for the free amides should ideally be those taken in the vapour state, but as these are available in only very few cases (owing to the low volatility of amides) we have had of necessity to use spectra measured in dilute solutions; in these cases it must therefore be remembered that the band shifts quoted are minimal values. As mentioned above, the spectrum of the cadmium chloride complex of *N*-methylacetamide has been considered [7] to indicate structure (II), but one of the main lines of evidence was the absence of large shifts as between complex and free amide. However, it was the liquid-amide spectrum (and not that of a dilute solution or gas) that was taken as reference and therefore the result is not surprising in terms of a structure analogous to (I), because one (hydrogen-bonded) carbonyl-associated form was being compared with another (" cadmium-bonded "). We refer to the data on this cadmium chloride complex in connection with Table 1.



(IV)

Structure (III) was considered because acylium ions are known and so is the hydroxyfluoroborate anion, $[HO{\cdot}BF_3]^-$, which can be considered to resemble the anion shown in (III). Nevertheless, this structure must be rejected because the amide complexes showed no absorption in the range 2200—2400 cm.$^{-1}$, whereas the acetylium ion, $[CH_3{\cdot}CO]^+$, has recently been characterised as having a strong carbonyl absorption at 2290 cm.$^{-1}$.[10]

(ii) *The* NH *stretching frequencies.* The results are shown in Table 1 (*a*). The points to note are: (i) dilution of the free amide causes large increases in ν_{NH}; (ii) the values shown for ν_{NH} of boron halide complexes in solution and paraffin mull are almost identical; (iii) the complexes have ν_{NH} at much lower frequencies than do solutions of the free amides; (iv) in primary amides a third NH stretching mode is apparent. The significance of (i)

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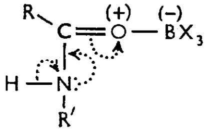
[8] Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1958, **29**, 611.

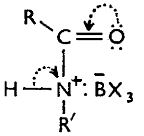
[9] Klemperer, Cronyn, Maki, and Pimentel, *J. Amer. Chem. Soc.*, 1954, **76**, 5846; Cannon, *Mikrochim. Acta*, 1955, 555.

[10] Susz and Wuhrmann, *Helv. Chim. Acta*, 1957, **40**, 722.

and (ii) has been discussed in the preceding section, and (iii) is consistent with structure (I) [see (V)], which requires the NH bond in the complex to be longer than in the free amide. However, it should be noted that, also for (II), a similar shift would be predicted [see (VI)].



(V)



(VI)

The appearance of an extra band in the primary amide complexes may be due to the existence of two geometrical isomers, although a fourth band would probably then be expected. Geometrical isomers in the complexes could arise from one of two causes: (i) from restricted rotation about the CN bond because its double-bond character exceeds that of the free amide (the hydrogen could then lie either *cis* or *trans* with respect to the carbonyl group); or (ii) from the mode of attachment of the boron halide molecule (either *cis* or *trans* with respect to the NHR group; see p. 2150). An increase in the number of NH stretching absorptions has been noted in certain transition-metal complexes with amines.[11]

(iii) *The amide I band.* The results are summarised in Table 1 (*b*). For the primary amides shown, no data on vapour-phase spectra appear to be available;[12] however, it is to be expected that the amide I band in unassociated acetamide and benzamide would fall at a frequency somewhat lower than 1740 cm.$^{-1}$, because this is the position of the amide I band in gaseous formamide, and the electron-releasing methyl and phenyl groups would lower the CO frequency. On the other hand, the value for acetamide is likely to be greater than that in *N*-methylacetamide (1718 cm.$^{-1}$). It should be noted that in general (i) dilution of the primary or secondary amide increases the frequency of the amide I band; (ii) the values shown for the boron halide and titanium tetrachloride complexes in solution and in paraffin mull are substantially the same; (iii) the amide I band for complexes is at lower frequencies than for solutions of free amides (primary and secondary); (iv) the magnitude of the shift varies considerably with structure, and for two of the tertiary amides is insignificant.

Problems (i) and (ii) have been discussed, and with regard to (iii) it must be remembered that the amide I band does not arise merely from the stretching vibration of the carbonyl group.[8] If it did, and structure (I) were correct, then a lowering in frequencies would be expected[13] for the complexes of 100—150 cm.$^{-1}$. For the primary and secondary amide complexes the shifts are 19—66 cm.$^{-1}$ (and probably of the order 70—100 cm.$^{-1}$ if compared with unassociated amides) and this seems consistent with structure (I), whilst structure (II) would require a shift in the opposite direction [see (VI)].

The two aliphatic tertiary amides present a difficulty. The free amides cannot associate and therefore the position of the amide I band should be independent of the state of molecular aggregation. A possible explanation can be put forward. In the free amides, the groups attached to nitrogen profoundly influence the position of the amide I band, and electron-releasing (conjugative or hyperconjugative) groups cause absorption at lower frequencies (*e.g.*, in formamide at 1740 cm.$^{-1}$,[14] *N*-methylformamide at 1724 cm.$^{-1}$,[15] and *NN*-dimethylformamide at 1675 cm.$^{-1}$). In the corresponding complexes, similar electron-release requires coplanarity of the groups attached to nitrogen with the N, C, O, B atoms and this may be sterically difficult. The exceptionally large shift with *NN*-diphenylacetamide would thus be accounted for on the basis that in the free amide

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[11] Chatt, Duncanson, and Venanzi, *J.*, 1956, 2712.
[12] Muetterties and Rochow, *J. Amer. Chem. Soc.*, 1953, **75**, 490.
[13] Lappert, Paper presented at International Conference on Co-ordination Chemistry, London, 1959.
[14] Evans, *J. Chem. Phys.*, 1954, **22**, 1228.
[15] Jones, *Mol. Spectroscopy*, 1958, **2**, 581.

itself (as in its complex) coplanarity is not attained, and the reason for the virtual identity of values for amide I bands in *NN*-dimethylformamide and acetamide complexes could then be explained on the view that the shift caused by the acceptor molecule's exercising its effect is neutralised by the decrease in the contribution made by the groups attached to nitrogen. On the other hand, the nuclear magnetic resonance spectrum (see below) of *NN*-dimethylformamide shows that $H{\cdot}CO{\cdot}NMe_2$ is virtually coplanar.

(iv) *The amide II band.* The results are summarised in Table 1 (*c*). For some of the other amides, selection of particular bands as the amide II was considered unsafe. Very large shifts in the amide II absorptions of the free amide are observed and depend on changes in state. This is particularly clear for *N*-methylacetamide, where the value for the gaseous substance is available, and one may conclude that increase in hydrogen-bonding is accompanied by a large increase in frequency of amide II absorption. On the other hand, for the amide complexes such shifts do not appear and this is again consistent with structure (I).

(v) *The amide III band.* The results are summarised in Table 1 (*d*) and the observations are similar to those for the amide II band. The complexes have amide III bands at even higher frequencies than the fully hydrogen-bonded amides, in which such bonding increases the absorption frequency. The shifts to higher frequencies for complexes are again to be expected in the light of structure (I), because ν_{CN} and δ_{NH} make the major contribution to the amide III band. The remaining contribution (20%) comes from the CH deformation mode in the ketonic methyl group, and on no structure (except III) would one expect this mode to be influenced significantly by co-ordination.

(vi) *The amide V band.* No bands appear in the spectra of the amide complexes which can be attributed to the NH out-of-plane bending mode. However, the absence of such a band in the spectrum of the cadmium chloride complex of *N*-methylacetamide has been taken as evidence for structure (II). We do not share this view, because also on the basis of (I) we should expect the band to change in intensity and position, for the NH bond in (I) [see (V)] as in (II) [see (VI)] is lengthened on co-ordination. Our comparisons throughout have been with the unassociated free amide and, with regard to the amide V band of -methylacetamide, in the vapour phase this should lie outside the sodium chloride range. In support of this view—for the value is not in the literature—we note that the amide V band in the free amide appears at 790 (crystal, $-60°$), 745 (crystal, $+15°$), 725 (liquid), and 648 cm.$^{-1}$ (dilute non-polar solution).[16]

(vii) *The* CH *deformation* (*in* $CH_3{\cdot}N<$). The results shown in Table 1(*e*) indicate that the absorption band shows no significant difference as between free amide and complex. The CH deformations in methyl groups are considerably influenced by the electronegativity of adjacent atoms [17] (*e.g.*, $\nu_2 = 1475, 1355, 1305$, and 1251 cm.$^{-1}$ in methyl fluoride, chloride, bromide, and iodide, respectively) and in terms of structure (II) a shift to higher frequency would have been expected.

(viii) *The tertiary amides and complexes.* For *NN*-dimethylformamide, assignments for certain bands at 1661 (amide I), 1255 [CN (contiguous to carbonyl) stretch], 1091 [CN (contiguous to methyl) stretch], and 1389 cm.$^{-1}$ [CH (in $CH_3{\cdot}N<$) deformation] can be made, mainly by analogy with ester assignments.[18] The boron trichloride complex, however, shows much increased absorption in this region (see Table 8), and only the amide I band (1686 cm.$^{-1}$) can be assigned with confidence. This increase in complexity of the spectrum may be associated with the increased possibilities of geometrical isomerism in the co-ordination compound.

With *NN*-dimethylacetamide, the position appears to be clearer and the results with tentative assignments are shown in Table 2; the failure to observe significant shifts may be accounted for on the basis of the argument put forward for the amide I band.

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[16] Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1956, **24**, 408.

[17] Bellamy and Williams, *J.*, 1956, 2753.

[18] Thompson and Torkington, *J.*, 1945, 640.

TABLE 2. NN-*Dimethylacetamide and complexes.**

Amide (liquid)	BCl_3 Complex (dil. soln. in CH_2Cl_2)	BBr_3 Complex (dil. soln. in CH_2Cl_2)	Tentative assignment
1634	1633	1637	Amide I
1269	1255 †	1263 †	ν_{CN} (of $-CO\cdot N<$)
1011	995	996	ν_{CN} (of $>NMe$)
1399	1401	1399	δ_{Me} (of $>NMe$)
1497	1481	1475	δ_{Me} (of $Me\cdot C\lessgtr$)
1361	1370	1374	

* These results show deviations of ±5 cm.$^{-1}$.

† From spectra in paraffin mulls, as methylene chloride absorbs in this region.

With *NN*-diphenylacetamide and its boron trichloride complex, the amide I band can readily be detected (section iii). It may also be significant that aromatic CH out-of-plane deformations appear as doublets at 775 and 765 cm.$^{-1}$ (free amide) and at 772 and 761 cm.$^{-1}$ (complex). This could be interpreted as implying double-bond character in the CN bond (of $-CO\cdot N<$) in both amide and complex and would thus be consistent with structure (I).

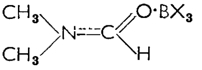
(ix) *The* BCl *and* BBr *stretching modes.* These are shown in Table 3. Undoubtedly, further absorption bands (particularly for the boron tribromide complexes) could be detected if their spectra were examined in the potassium bromide region. As is to be expected, the bands lie at lower frequency than for tervalent boron compounds, such as boron trichloride (958 and 924 cm.$^{-1}$) and tribromide (806 and 743 cm.$^{-1}$).[19]

Nuclear Magnetic Resonance Spectra.—(i) NN-*Dimethylformamide–boron trichloride.* The spectrum (of a methylene chloride solution) shows two lines in the region expected from the protons of the NMe_2 group; these lines are of equal intensity and the separation between them is 0·11 p.p.m. This separation was shown to be a chemical shift between non-equivalent protons by measurements at 40 and 56 Mc./sec., which showed it to be field-dependent. The presence of two lines can be reasonably interpreted (as it has been in the free amide [20] and the hydrochloride [5]) as caused by the presence of two different methyl groups in a structure (VII) having restricted rotation about the C–N (of the $-CO\cdot N<$ group) bond. Chemical shifts of similar magnitudes have been found between protons of the methyl groups in 1,1-dimethyl-olefins which are unsymmetrically substituted at $C_{(2)}$.[21] Each of the two lines is a doublet, the separations being $0{\cdot}8_3$ and $1{\cdot}3_2$ c.p.s., for the low- and the high-field line, respectively. Presumably, the doublet structure is produced by the indirect spin–spin coupling interaction between the methyl-protons and the aldehydic proton. The observation of splitting of this order of magnitude across four bonds (H–C–N–C–H) is consistent with the view that there is some appreciable double-bond character in the C–N (of the $-CO\cdot N<$) bond. Splitting of about this value has been observed with appropriate olefins.[21] The aldehydic proton shows resonance of some complexity, but it was not possible to determine whether this was a septuplet, as would be expected from spin–spin coupling.

TABLE 3. BX *Assignment in boron halide–amide complexes.**

Compound	γ_{BX} (cm.$^{-1}$)	Compound	ν_{BX} (cm.$^{-1}$)
$CH_3\cdot CO\cdot NH_2,BCl_3$	803, 773, 734	$H\cdot CO\cdot NMe_2,BCl_3$	784, 750, 699
$CH_3\cdot CO\cdot NHMe,BCl_3$	786, 762	$CH_3\cdot CO\cdot NH_2,BBr_3$	683
$CH_3\cdot CO\cdot NMe_2,BCl_3$	777, 753, 713	$CH_3\cdot CO\cdot NHMe,BBr_3$	674

* These results show deviations of ±2 cm.$^{-1}$ and are on paraffin mulls.



(VII)

The observation of a chemical shift in *NN*-dimethylformamide–boron trichloride is consistent with structure (I), but not (II), as the molecule would not then be planar

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[19] Anderson, Lassettre, and Yost, *J. Chem. Phys.*, 1936, **4**, 703.

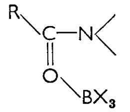
[20] Phillips, *J. Chem. Phys.*, 1955, **23**, 1363; Gutowsky and Holm, *ibid.*, 1956, **25**, 1228.

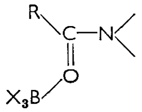
[21] Jackman and Wiley, *Proc. Chem. Soc.*, 1958, 196.

(nitrogen, *sp*^{3}-hybridised), whilst the spin–spin coupling, which is not shown by the free amide[20] or its hydrochloride,[5] shows that CN bond order is significantly increased on co-ordination, as required by structure (I) [see (V)].

(ii) NN-*Dimethylacetamide and its boron trichloride complex.* The free amide, unlike the corresponding formamide,[20] shows a single line for the methyl-protons of the NMe_2 group, whilst the complex shows some signs of a chemical shift (the separation is slight and not symmetrical). This suggests that substitution of the aldehydic proton in the formamide by the ketonic methyl group of the acetamide prevents coplanarity of the molecule.

(VIII)





(IX)

Stereochemistry of the Complexes.—Apart from the problem of restricted rotation about the CN bond, discussed in the preceding section, the question of the orientation of the halide molecule has to be considered. As postulated for ester and ketone complexes,[13] it is likely that the oxygen atom of the carbonyl group has hybridisation approximating to *sp*^{2}, and this permits alternative orientations (VIII) and (IX). We have no direct evidence as to this point, but, as discussed above, certain observation on infrared spectra would be consistent with this view.

Comparison of the Two Boron Halide Systems.—In general, it will be seen that infrared spectroscopic shifts for boron trichloride complexes are of the same order of magnitude as for the tribromide analogues. Shifts for the bromide would have been expected to be slightly greater than for the trichloride by analogy with observations on ester complexes,[13] which were interpreted as showing that the tribromide is a better acceptor than the trichloride.

Experimental.—Compounds were prepared and purified as described in a previous paper.[1] The essential results have been given but are supplemented by Table 4 (max. in cm.$^{-1}$;

TABLE 4. *Absorption bands* (900—1700 *cm.*$^{-1}$) *in amide complexes.*[a]

$H\cdot CO\cdot NMe_2$, BCl_3	$CH_3\cdot CO\cdot NH_2$, BCl_3	$CH_3\cdot CO\cdot NH_2$, BBr_3	$CH_3\cdot CO\cdot NHMe$, BCl_3	$CH_3\cdot CO\cdot NHMe$, BBr_3	$CH_3\cdot CO\cdot NMe_2$, BCl_3
1686s [b]	1661s [b]	1658s [b]	1650s [b]	1645s [b]	1633s [b]
1481w	1550s [c]	1546m [c]	1538s [c]	1536m	1481m
1458m	1490s	1488s	1408s [e]	1406m [e]	1401s [e]
1429m	1414m	1412s	1381m	1357w	1370s
1391m	1374m	1372w	1323s [d]	1323m [d]	1255s
1332s	1104s	1103s	1174s	1174m	1036w
1248m	1043m	1046w	1083w	1085w	995s
1136w	1028m	1026w	1020w	1026m	
1058w	926s		957m	964m	
992w					
901s					

$CH_3\cdot CO\cdot NMe_2$, BBr_3	$CH_3\cdot CO\cdot NHPh$, BCl_3	$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$-*p*	$CH_3\cdot CO\cdot NPh_2$, BCl_3	$Ph\cdot CO\cdot NH_2$, BCl_3
1635s [b]	1626s [b]	1623s	1600w	1647s [b]
1475s	1587s	1590m	1553s [b]	1597m
1399s [e]	1553m [c]	1550m [c]	1497s	1563m
1374m	1459m	1513s	1477s	1309w
1263s	1433m	1443m	1408m	1190w
1023w	1370m [d]	1425m	1377m	1152m
996m	1038m	1368m	1217m	1105m
	952m	1245m	1079w	1072m
		1172m	1038m	1003w
		1109w	1015m	935w
		957w	913w	

[a] Dil. solution n CH_2Cl_2. [b] Amide I. [c] Amide II. [d] Amide III. [e] CH deformation (in Me·N<) mode.

s = strong; m = medium; w = weak). Measurements were taken on a Grubb–Parsons S3A double-beam spectrometer with rock-salt optics and calibrated throughout its range by using water, ammonia, and carbon dioxide as standards. It may be significant that spectra of complexes showed sharper bands than those of free amides.

High-resolution nuclear magnetic resonance spectra were measured on a Varian Associates Model 4300B spectrometer with superstabiliser.

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