

PHYSICAL PROPERTIES AND STRUCTURE OF DONOR-ACCEPTOR COMPLEXES

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Modern coordination chemistry has at its disposal a large range of techniques for investigating the structure of addition compounds. Some of these rely on the chemical reactions of complexes but the majority depend on the interpretation of results obtained by measuring certain physical properties. It is important at the outset to distinguish between two types of property: macroscopic and molecular. Macroscopic properties include the following:

- (a) melting point, boiling point, and entropy of evaporation, which normally yield little information of structural importance;
- (b) density, surface tension, refractive index, and viscosity, which lead to the molar volume, parachor, molar refractivity, and Batschinski's constant; these are all to some extent indications of molecular size but are all notoriously difficult to interpret unambiguously in terms of specific structures;
- (c) dipole moment and electrical conductivity, which in favourable cases yield important information about symmetry and the presence or absence of ions, and which can frequently be used diagnostically to decide between alternative structures;
- (d) paramagnetic susceptibility, which concerns unpaired non-bonding electrons but which can be used in certain circumstances to make deductions about structure.

Molecular properties, by contrast, yield much more intimate information about the structure of the species present in the compounds. Three broad classes of technique can be distinguished, namely: spectroscopic, diffraction, and resonance techniques. Spectroscopy embraces

- (a) ultra-violet and visible spectra, which are concerned with the transitions of valency electrons and loosely held non-bonding electrons between various energy levels;
- (b) infra-red and Raman spectra, which give detailed information about molecular symmetry and the presence of characteristic groups of atoms;
- (c) microwave spectra, which, at least for simple gases, can indicate the molecular configuration and give precise information about the exact dimensions of the molecule; and
- (d) polarimetry and optical rotatory dispersion, which are applicable for asymmetric molecules.

Diffraction techniques comprise X-ray diffraction, electron diffraction, and neutron diffraction techniques and the range of applicability of each is

now generally well understood. The most recent additions to the armoury of techniques available to the coordination chemist are nuclear magnetic resonance, nuclear quadrupole resonance, electron spin resonance, and the resonant absorption of γ -rays emitted without recoil in the Mössbauer Effect.

Not all of these methods are applicable to any given problem. For instance, in investigating the structure of boron trifluoride dihydrate, which is a colourless liquid at room temperature, none of the diffraction or resonance techniques with the exception of n.m.r. is applicable, and little information can be obtained from the visible spectrum or from magnetochemistry. This leaves vibrational spectroscopy and some of the macroscopic methods, such as conductivity and electrolysis.

It is also important to note that some of the macroscopic properties, particularly conductivity, are extraordinarily sensitive to small concentrations of minor species in equilibrium with the bulk of the liquid, and that such species are almost impossible to detect by spectroscopic, diffraction, or resonance techniques. The most familiar examples of this are the ions formed by self-dissociation of solvents such as water and liquid ammonia. It is, therefore, worthwhile to review the type of information obtainable from these classical, macroscopic techniques since this is frequently complementary to the data obtained from the more recent molecular techniques.

I shall confine my examples to the properties of simple molecular addition compounds since these have unique importance for two very different reasons. Firstly, and this may come as a surprise, these complexes are ideally suited for studying electrical conduction phenomena in the fused state, and are, thus, model compounds for molten salts which can be studied at room temperature or slightly above. Secondly, these adducts are model compounds for coordination chemistry as a whole, since one can study the effect of forming just one bond at a time and, thus, go a long way to isolating the various factors affecting the stability of the bond.

Let us consider the conductivity first. If boron trifluoride is bubbled into a ligand such as an alcohol, fatty acid, ester, or ether in a weighed conductivity cell it is found that the conductivity rapidly increases by several powers of 10 to a maximum and then drops slightly to a minimum near the 1:1 ratio¹; *e.g.*, for acetic acid, the conductivity of the adduct is 2×10^5 times greater than the conductivity of the pure ligand itself. In other words, the formation of a donor-acceptor bond causes such drastic reorganization of the electron charge distribution within the molecule that the complex ionizes. This need not cause surprise since donor-acceptor reactions, such as $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4^+\text{Cl}^-$ are well known, but it does mean that the possibility of ionic dissociation must always be considered when discussing the structure of molecular addition compounds. Sometimes conductivity-composition isotherms indicate the presence of more than one compound; thus, the system boron trifluoride-methanol shows conductivity minima both at the 1:2 and the 1:1 ratio. There is no theoretical reason why the minima should occur precisely at stoichiometric ratios since the observed conductivity depends on a variety of factors. However, the existence of a minimum is strong presumptive evidence for complex formation which can then be checked by other means. Conversely, the absence of a minimum

PROPERTIES AND STRUCTURE OF DONOR-ACCEPTOR COMPLEXES

does not necessarily imply the absence of a compound since subsidiary factors, such as viscosity, may be altering so rapidly as to obscure a minimum.

Perhaps it should be mentioned that the existence of a measurable conductivity does not necessarily imply self-dissociation into ions since conductivity in general can also conceivably arise from ionic dissociation of dissolved impurities, from semi-conductivity, or from metallic conductivity. However, the fact that the molten complexes have well-defined decomposition potentials and satisfy Faraday's Laws of electrolysis eliminate the last two possibilities, and conduction cannot be due to impurities since this is reproducible by several techniques of sample preparation, and would, in some cases, imply concentrations as high as 5 molar of a fully ionized impurity. The shape of the conductivity-composition curves and the fact that the separate donor and acceptor moieties have negligible conductivity also argues against any other interpretation than ionic self-dissociation of the complexes.

Clearly it is important to develop a method for calculating the degrees of ionic dissociation in such molten complexes. It is possible to gain an idea of the order of magnitude of the concentration of ions by considering conduction to be due to the normal independent migration of ions whose mobility is controlled by their size and charge and by the viscosity of the medium. The derivation² considers the specific conductivity, κ , to depend on the number of cations and anions (n_+ , n_-), their mobility (v_+ , v_-) and the electronic charge, e :

$$\kappa = n_+ev_+ + n_-ev_-$$

For a 1:1 electrolyte $n_+ = n_-$ and the average mobility v is $\frac{1}{2}(v_+ + v_-)$. Hence $\kappa = 2nev$ where n is the number of current carriers of one sign per ml

i.e.
$$n = \kappa/2ev \text{ per ml} = M\kappa/(2d\epsilon v) \text{ per mole,}$$

where M is the molecular weight and d the density. Hence, the ratio of the number of ions of one sign to the original number of molecules:

$$\frac{n}{N} = \frac{M\kappa}{2Nde v}$$

The only unknown on the right hand side is v , the average mobility. In the absence of experimental values it is possible to estimate the mobility and so get an idea of the degree of dissociation (α), because mobilities of ions fall within a narrow range of values. Moreover, they are approximately inversely proportional to the viscosity (Walden's Rule); *i.e.*, $v = v_0/\eta$ where v_0 is a standard, average mobility in a medium of viscosity 1 cp. Hence:

$$\alpha \% = \frac{100n}{N} = \frac{M\kappa\eta}{d} \cdot \frac{100}{2Nev_0}$$

Now, and this is the crux of the argument, reference to tables of mobilities of ions in water (1 cp) shows that all except H^+ and OH^- fall in the range $(2.5 - 10) \times 10^{-4} \text{ cm}^2\text{sec}^{-1} \text{ V}^{-1}$. There will, doubtless, be some error in calculating mobilities in other media from those in water simply by scaling

down by the relative viscosity of the medium because of the changing solvation of the ionic species. But even in melts, the same sort of ionic migration process is occurring and the error, whilst there, is unlikely to be much as 100 per cent and certainly not an order of magnitude. Hence, for an order of magnitude calculation, since we have no experimental mobilities, we can assume $v_0 = 5 \times 10^{-4}$. When this is corrected for viscosity it will probably represent the mobility of all the ions considered to within a factor of 2-3. Substituting this and other values in the expression one finds, conveniently, that $100/2Nev_0 \simeq 1$, so that

$$\alpha \text{ \%} \simeq \frac{M\kappa\eta}{d} = \mu\eta$$

where μ is the molar conductivity, $M\kappa/d$.

In short, to estimate the degree of ionic dissociation it is necessary to know the specific conductivity, the density, and the viscosity of a molten compound. We have measured these properties for a wide variety of adducts of boron and gallium trihalides under vacuum conditions which exclude adventitious contamination with moisture or other impurities. Some of these results^{2, 3} are shown in *Table 1*. It can be seen that the degree of dissociation varies

Table 1. Some typical values of $\mu\eta$ ($\text{ohm}^{-1}\text{cm}^2 \text{ cp mole}^{-1}$)

$\text{BF}_3 \cdot 2\text{H}_2\text{O}$	28.4	$\text{BF}_3 \cdot \text{Et}_2\text{O}$	0.071
$\text{BF}_3 \cdot \text{H}_2\text{O}$	10.5	$\text{BF}_3 \cdot \text{Me}_3\text{N}$	0.34
$\text{BF}_3 \cdot \text{MeOH}$	2.22		
$\text{BF}_3 \cdot 2\text{ROH}$	3-8		
$\text{BF}_3 \cdot \text{MeCO}_2\text{H}$	4.7	$\text{BCl}_3 \cdot \text{py}$	0.79
$\text{BF}_3 \cdot \text{MeCO}_2\text{R}$	0.04-0.2	$\text{BCl}_3 \cdot \text{pip}$	0.69

from about 30 per cent for boron trifluoride dihydrate through values of about 1-10 per cent for the alcoholates and acetic acid complex to about 0.1 per cent for esters and the etherate. Boron trichloride complexes with pyridine and piperidine also have values of $\mu\eta$ corresponding to about 1 per cent dissociation into kinetically free ions.

Having thus established that many simple molecular addition compounds are appreciably dissociated into ions it was interesting to discover whether some complexes had values of conductivity, viscosity, and density which implied complete dissociation as molten salts. This would have the great advantage that such compounds could be used as models for molten salts at much lower temperatures than are normally required for such systems, because many of these complexes melt in the range 0-150°. Examples of such completely dissociated complexes emerged during a study of the lower valent states of gallium. Gallium dichloride and dibromide are both diamagnetic, and Raman spectroscopy^{4, 5} shows that the molten compounds are, in fact, ionic and consist of an equal number of ions in which gallium is univalent and trivalent, *e.g.* $\text{Ga}^+\text{GaBr}_4^-$. This is reflected in the values of their reduced conductivity shown in *Table 2*. Values of $\mu\eta$ are seen to be of the order of 100 per cent implying complete dissociation into ions. The

PROPERTIES AND STRUCTURE OF DONOR-ACCEPTOR COMPLEXES

dihalides are, therefore, complexes of univalent gallium and form an interesting example of the stabilization of a lower valency by coordination since the ion which is stabilized (Ga^+) is not the one which is coordinated. Other complexes of gallium so far investigated in the molten state⁶ are considerably less dissociated into ions, typical values of $\mu\eta$ being in the range $\frac{1}{2}$ –4 per cent.

Table 2. Reduced conductivity of some complexes of gallium trihalides

Compound	$\mu\eta$	Compound	$\mu\eta$
$\text{GaCl}_3 \cdot \text{GaCl}$	103.3	$\text{GaBr}_3 \cdot \text{GaBr}$	136.3
$\text{GaCl}_3 \cdot \text{POCl}_3$	0.44	$\text{GaBr}_3 \cdot \text{POBr}_3$	1.0
$\text{GaCl}_3 \cdot \text{py}$	2.15	$\text{GaBr}_3 \cdot \text{py}$	3.1
$\text{GaCl}_3 \cdot \text{pip}$	3.26	$\text{GaBr}_3 \cdot \text{pip}$	3.9

By measuring the conductivity, viscosity, and density over a range of temperature, activation energies can be obtained, and values are usually in the range 4–6 kcal/mole¹,⁶ typical of molten salts. The activation energies of conduction and viscous flow are approximately equal, the mean value of E_η/E_μ for 19 complexes of boron being 1.02 and for 10 complexes of gallium 1.08. Little point would be served in discussing all these values in detail but perhaps some indication of the way they can be analysed further in terms of typical molten salt parameters can be seen from Table 3.

Table 3. Conduction parameters for gallium dihalides

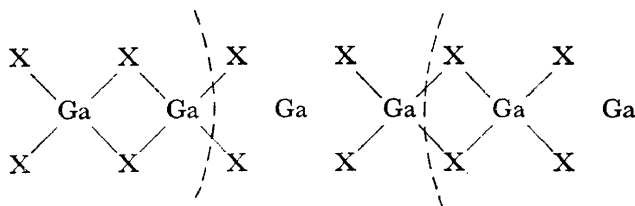
	$\text{Ga}^+\text{GaCl}_4^-$	$\text{Ga}^+\text{GaBr}_4^-$	Ag^+NO_3^-
$\mu\eta$	103	136	136
E_η	4.7	5.3	3.9
E_μ	3.8	4.2	3.2
E_η/E_μ	1.23	1.27	1.24

The reduced conductivity is similar to that of molten silver nitrate and, as already seen, implies complete dissociation into ions. The ratio of the activation energies suggests that, whereas viscous flow involves the shear of large anions over each other, conduction occurs more readily by the rapid migration of the small cation through interstices in the anion network. These ideas also permit the interpretation of two otherwise rather puzzling observations⁷:

(i) Dissolution of gallium in gallium dichloride, decreases the conductivity despite the fact that the reaction $\text{Ga}^+\text{GaCl}_4^- + 2\text{Ga} \rightarrow 4\text{Ga}^+\text{Cl}^-$ increases the number of ions. The decrease in conductivity is due to the partial collapse of the anion lattice and the replacement of GaCl_4^- anions by Cl^- anions which are comparable in size to the gallous ions. This restricts the simple migration of gallous ions through the interstices of the anion network.

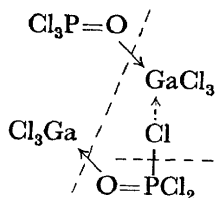
(ii) The reduced conductivity of the bromide is greater than that of the chloride. At first sight one might have expected the opposite since, although the cations are the same, the GaBr_4^- anion is larger than the GaCl_4^- anion and would, therefore, move more slowly. But the anions take little part in the migration process and it is easier for the gallous ions to move through the larger interstices of the larger GaBr_4^- ions. It should also be noted that, although the activation energy of conduction of the bromide is greater than that of the chloride, the ratio E_η/E_μ is also greater, implying that the bromide is conducting more easily than it would be expected to. The same appears to be true of molten salts in general, where there is a large disparity in size between cation and anion. Thus $\mu_\eta\text{AgCl} < \text{AgBr} < \text{AgI}$ (holes get larger); and $\mu_\eta\text{KCl} < \text{NaCl} < \text{LiCl}$ (cation becomes smaller). In short, μ_η increases for fully ionized salts as the ratio E_η/E_μ increases.

An interesting confirmation of these ideas comes from the molar volume of the gallium dihalides, which are exactly two-thirds of the molar volume of the corresponding trihalides. This implies that the two gram atoms (23 ml) of gallium metal used to reduce the trihalide fit into the existing holes of the liquid structure and cause no expansion of the melt, the factor two-thirds arising because 2 moles of the trihalide furnish 3 moles of the dihalide:

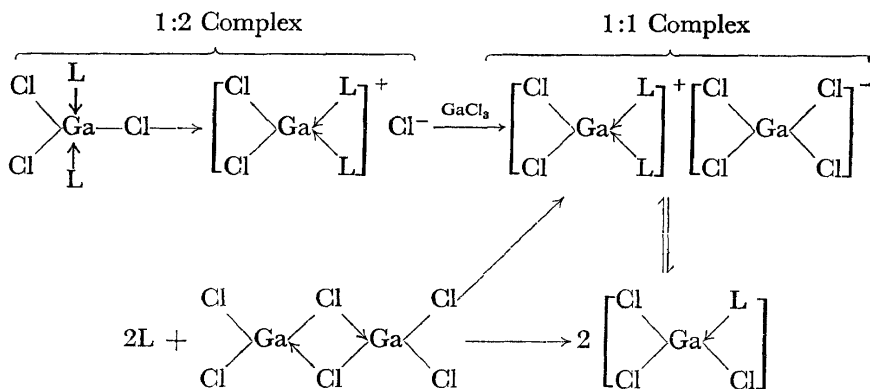


The mode of ionization of the gallium dihalides was elucidated without difficulty by Raman spectroscopy since GaX_4^- was the only polyatomic species in the melt. Such an unambiguous answer is not possible with the complexes of boron and gallium trihalides since these are ionized only to the extent of about 1 per cent. This emphasizes the difficulty mentioned earlier in interpreting macroscopic properties since these give little intimate information about the detailed structure of a complex. Electrolysis experiments are frequently helpful in deciding which atoms are in the cation and which in the anion and they have been used successfully for several boron trifluoride complexes¹. However, they have yielded less information on the gallium complexes because of the involatility of the electrolysis products. Perhaps two examples will make the problem clearer.

The Raman spectrum of fused $\text{GaCl}_3 \cdot \text{POCl}_3$ has been interpreted⁸ in terms of the covalent adduct $\text{Cl}_3\text{PO} \rightarrow \text{GaCl}_3$ and this is undoubtedly the predominant species in the melt. However, the conductivity data in *Table 2* suggest that, in addition, there is about $\frac{1}{2}$ per cent of free ions and it is unlikely that the Raman lines from these species will be detectable in the presence of 99.5 per cent of the undissociated complex, particularly as the positions of several of the lines from both structures will be similar. It is possible that a small equilibrium concentration of ions such as POCl_2^+ and GaCl_4^- could be formed in this system by a ligand-switch rearrangement of the type illustrated below, though there is no direct evidence for this.



The second example concerns the complexes of gallium trihalides with pyridine and piperidine. The absence of gaseous products when the molten 1:1 and 1:2 adducts are electrolysed eliminates the possibility that the complexes ionize as $\text{H}^+[\text{C}_5\text{H}_4\text{N} \rightarrow \text{GaCl}_3]^-$ and $[\text{C}_5\text{H}_5\text{NH}]^+[\text{C}_5\text{H}_4\text{N} \rightarrow \text{GaCl}_3]^-$; such a formulation would also imply that the adduct with two moles of ligand would be more stable than the 1:1 complex whereas the reverse is true. This contrasts with the adducts of boron trifluoride where the 1:2 complexes are always more stable than the 1:1 and suggests that the gallium complexes have a different structure. An obvious possibility is that the 1:2 complexes in this case are 5-coordinate and that there is an ionization equilibrium as shown below. The 1:2 complex ionizes by rearrangement of the



gallium from trigonal bipyramidal to tetrahedral configuration with elimination of a chloride ion and this ion can donate to a further GaCl_3 unit to give the ionic 1:1 complex. This interprets the ionization of the 1:2 complex and the greater stability of the 1:1 compound. The direct formation of the 1:1 complex from Ga_2Cl_6 and 2 moles of ligand (lower line) would involve a replacement of bridged chlorine donors by either one or two moles of ligand to give the ionic and covalent forms of the 1:1 complex respectively. On this basis the ionization equilibrium of the 1:1 complex itself (shown as the vertical equilibrium on the right hand side of the diagram) involves a ligand replacement reaction of precisely the same kind as that proposed above for the complex $\text{GaCl}_3 \cdot \text{POCl}_3$. These examples demonstrate quite clearly the use of conductivity in establishing the presence of minor constituents in equilibrium with the bulk of the complex but also demonstrate the speculative nature of conclusions about the precise structure of the ionic species, and the need to use a range of complementary techniques.

Even more speculative are the conclusions to be drawn from viscosity data alone. The diagnostic use of viscosity is based on an equation first proposed 50 years ago by Batschinski⁹ who pointed out that the viscosity of many organic compounds was inversely proportional to their specific volume over wide ranges of temperature:

$$\eta = B/(v - b)$$

We have verified this equation empirically for a large range of inorganic liquids and fused complexes. The speculation arises when attempts are made to interpret the constants B and b in terms of specific physical concepts. Thus, one can imagine that viscosity should be directly proportional to the free volume which enables a molecule to move from one position to another in the liquid. On this basis, b represents the specific volume of the solid at the m.p. since at this temperature the free volume becomes effectively zero and the viscosity becomes infinite. Likewise B would be proportional to the size of flow units and would permit structural deductions to be made. Both correlations are born out for a large number of inorganic liquids but disconcerting exceptions occur sufficiently frequently to prevent confident deductions being made. For example, some typical values of Batschinski's constant are given in *Table 4*. B for piperidine is larger than for pyridine

Table 4. Values of Batschinski's constant
($10^2 B$ cp ml g⁻¹ mole⁻¹)

Ga ₂ Cl ₆	5.75	GaCl ₃ ·py	7.63	GaBr ₃ ·py	8.86
Pyridine	6.43	GaCl ₃ ·pip	10.6	GaBr ₃ ·pip	9.86
Piperidine	8.50	GaCl ₃ ·2pip	14.6	Ga ₂ Br ₆	5.60

due to ring buckling, and both values show the expected increase on complex formation. Moreover, the 1:2 piperidine complex with the postulated trigonal bipyramidal structure is larger than the tetrahedral 1:1 complex. In the final column, the B -values for the gallium tribromide complexes are larger than for the bromide itself, and the piperidine complex has a larger value than the pyridine adduct. However, gallium tribromide and its piperidine complex both have smaller B -values than the corresponding chlorides, whereas the reverse is true for the pyridine complex. It seems to be fairly generally true that inorganic bromides have smaller Batschinski constants than the corresponding chlorides and this is hard to correlate with the known larger size of bromine. Flow units, of course, need not be of molecular dimensions but there is no evidence from other sources that liquids such as arsenic trichloride, phosphorus trichloride, and phosphorus oxychloride are considerably more associated than the corresponding bromides. We must conclude that little confidence can be placed in the general applicability of this method for deducing the sizes of ionic or molecular species in the melt.

In discussing the conductivity, viscosity, and density of complexes so far, it has been assumed that electrical conduction occurs by the normal migration of ions. This is not always so and it is instructive to consider systems

PROPERTIES AND STRUCTURE OF DONOR-ACCEPTOR COMPLEXES

in which conduction can occur by a proton-switch type of mechanism, and the ways in which donor-acceptor complexes can be used to elucidate details of this behaviour. The most familiar example of a proton-switch occurs in water where the hydrogen ion and hydroxyl ion have mobilities which are considerably higher than those of other ions in aqueous solution. Another example is anhydrous sulphuric acid, but such systems are rare and we were interested in extending the range of substances which showed this phenomenon in order to define more closely the conditions which were necessary for a liquid to conduct by proton-switch¹⁰. The argument used can be illustrated by the data in *Table 5*. Boron trifluoride dihydrate is very substantially dissociated into ions at room temperature and when the hydrogen

Table 5. Reduced conductivity of hydro- and deuterio-compounds

<i>Compound</i>	<i>Structure</i>	$\mu\eta$ at 25°
BF ₃ ·2H ₂ O	H ₃ O ⁺ +BF ₃ OH ⁻	28·0
BF ₃ ·2D ₂ O	D ₃ O ⁺ +BF ₃ OD ⁻	28·2
H ₃ PO ₄	Hydrogen bonded	434·1
D ₃ PO ₄	Deuterium bonded	346·5

is substituted by deuterium the reduced conductivity remains unaltered since the size and mass of the ions which are migrating are very little affected. With phosphoric acid the picture is quite different; even if the compound is assumed to be completely dissociated into ions, these ions would have to move some four or five times faster than normal to account for the value of $\mu\eta$ (*cf.* the hydrogen ion in water which moves six times faster than expected). However, phosphoric acid is not a molten salt which means that the degree of ionization is much less than 100 per cent and the apparent mobility must be very much higher than normal. It is also apparent that, when hydrogen is replaced by deuterium, the conductivity drops dramatically. These facts are understandable in terms of a switch mechanism since the activation energy for a deutron-switch process is greater than for a proton-switch process. As the conductivity is no longer directly dependent on the rate of migration of ions and hence on viscosity it is not surprising that the activation energies for conduction (6·1, 6·5 kcal) differ markedly from the activation energy for viscous flow (7·92, 8·55 kcal). These experiments imply that phosphoric acid conducts by a proton-switch mechanism and this was proved beyond doubt by the electrolysis of potassium dihydrogen phosphate in fused phosphoric acid; the potassium ions did not migrate through the viscous liquid at all, the electricity being carried entirely by a proton-switch involving the biphosphate ion and the phosphoric acid hydrogen-bonded network. If it were possible to break all the hydrogen bonds by blocking the lone pairs on the oxygen atoms with an electron-pair acceptor such as boron trifluoride, then the viscosity would be expected to drop because the liquid would no longer be so heavily hydrogen-bonded, and the conductivity would also drop because the proton-switch mechanism would be replaced by a normal ionic migration process. Moreover, the replacement

of hydrogen by deuterium would have little or no effect on the conduction characteristics of the complex since conductivity would be by migration of ions as in boron trifluoride dihydrate. This is precisely what happens, as seen from *Table 6*. The conductivity of the hydrogen and deuterium complexes are virtually identical and the activation energies for viscous flow and

Table 6. Conduction characteristics of BF_3 complexes of phosphoric and tri-deutero-phosphoric acids

<i>Property</i>	H_3PO_4	D_3PO_4	$\text{H}_3\text{PO}_4\cdot\text{BF}_3$	$\text{D}_3\text{PO}_4\cdot\text{BF}_3$
m.p. ($^\circ\text{C}$)	42.35	45.95	ca. -100	ca. -100
$10^2\kappa_{25}$ ($\text{ohm}^{-1}\text{ cm}^{-1}$)	4.68	2.82	0.823	0.820
η_{25} (cp)	177.4	231.8	46.2	48.5
$\mu\eta$	434.1	346.5	33.5	35.3

conduction become very similar, implying that migration of ions through the viscous medium is the rate-determining process. The numerical data also suggest that the complexes are very considerably dissociated into ions.

This paper, so far, has attempted to show how the measurement of certain macroscopic properties can lead to important deductions about the structure of donor-acceptor compounds and how coordination complexes can be used as models for a variety of molten salt phenomena. Three main aspects have been considered:

- the estimation of the concentration of ions formed by the self-dissociation of fused complexes;
- the structure of the ions present; and
- the detailed mechanism of the conduction process.

A fourth aspect, which considers what factors decide whether a particular compound will be ionic or covalent is also important. This has been tackled by means of the thermochemistry of donor-acceptor adducts and the calculation of bond strengths, and some of the results obtained will now be briefly indicated.

The heat of formation of a crystalline complex can be found by measuring the heat evolved when the acceptor is dissolved in excess of the ligand and subtracting from this the heat of solution of the complex in a similar excess of ligand. These values, coupled with the heat of sublimation of the complex measured manometrically, give the heat of formation of gaseous adduct from gaseous donor and acceptor¹¹. The results in *Table 7* show that piperidine is a stronger ligand than pyridine (emphasizing the importance of

Table 7. Heats of reaction in kcal mole⁻¹

<i>Complex</i>	$-\Delta H_{\text{total}}$	$-\Delta H_{\text{soln}}$	$-\Delta H_f$ (cryst.)	$-\Delta H_f$ (gas)
$\text{BCl}_3\cdot\text{C}_5\text{H}_5\text{N}$	38.7	-2.0	40.7	37.9
$\text{BBr}_3\cdot\text{C}_5\text{H}_5\text{N}$	41.0	-4.5	45.5	43.5
$\text{BCl}_3\cdot\text{C}_5\text{H}_{10}\text{NH}$	122.7	38.3	84.4	80.6
$\text{BBr}_3\cdot\text{C}_5\text{H}_{10}\text{NH}$	163.1	48.6	114.5	111.6

PROPERTIES AND STRUCTURE OF DONOR-ACCEPTOR COMPLEXES

electron availability on the donor atom) and that boron tribromide evolves more heat than the trichloride (emphasizing the greater reorganization energy of the latter from planar to tetrahedral).

Similar studies on gallium halides are summarized in *Table 8*. Values

Table 8. Heats of formation in kcal mole⁻¹

<i>Complex (c)</i>	$-\Delta H$ (kcal mole ⁻¹)	<i>Complex (c)</i>	$-\Delta H$ (kcal mole ⁻¹)
GaCl ₃ ·AsCl ₃ (<i>l + c</i>)	1.4	GaCl ₃ ·Et ₂ O	9.3
GaCl ₃ ·PCl ₃ (<i>l + c</i>)	3.4	GaCl ₃ ·2Et ₂ O	15.5
GaCl ₃ ·POCl ₃	10.2	GaCl ₃ ·py	29.8
GaCl ₃ ·MeCOCl	4.1	GaCl ₃ ·2py	41.5
GaCl ₃ ·Me ₂ CO	15.3	GaCl ₃ ·pip	33.7
		GaCl ₃ ·2pip	52.1

range from 1 to 52 kcal and show clearly that a second mole of ligand is attached less strongly than the first. It is also apparent, as expected, that nitrogen donors are more exothermic than oxygen donors and that the incongruently melting complexes with arsenic and phosphorus trichlorides evolve little heat on formation. Values for the complexes with acetyl chloride and acetone reflect the fact that the negative inductive effect of chloride has reduced the electron availability at the oxygen atom to such an extent that chlorine, rather than oxygen is the donor atom, the complex being best formulated as acetyl tetrachlorogallate MeCO⁺GaCl₄⁻.

In favourable cases, the results lead for the first time to bond dissociation energies of gallium complexes⁶. Thus, when the gas-phase heats of formation of the complexes are corrected for the reorganization energy of the acceptor moiety on the basis of Cotton and Leto's calculations for boron and aluminium halides¹², then $D(N \rightarrow GaX_3) = 69.2$ kcal and $D(O \rightarrow GaCl_3) = 55.5$ kcal. These also imply $D(Cl \rightarrow GaCl_3) = 43$ kcal in the bridged dimer compared with a value of 86 kcal for $D(Ga-Cl)$ in planar monomeric GaCl₃. When the reorganization energy of 33 kcal is allowed for, the figures suggest that the bridge bonds are some 19 per cent weaker than the external bonds in the dimer.

This lecture began by pointing out that the modern coordination chemist has at his disposal a wide variety of techniques for investigating the structure of complexes. When applicable, spectroscopic, diffraction, and resonance techniques frequently provide intimate knowledge of the details of molecular structure. However, other properties, the so-called macroscopic properties, also furnish important information which is frequently complementary to

that obtained from molecular properties. The information obtainable from such properties has been reviewed and its range of applicability discussed so as to emphasize the care which should be taken in drawing detailed structural conclusions.

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