*Coordination Chemistry Reviews*
Elsevier Publishing Company, Amsterdam – Printed in the Netherlands

# THE USE OF CONDUCTIVITY MEASUREMENTS IN ORGANIC SOLVENTS FOR THE CHARACTERISATION OF COORDINATION COMPOUNDS

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(Received November 25th, 1970)

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## A. INTRODUCTION

The determination of conductance data for coordination compounds and the interpretation of such data in terms of possible structures dates back to the commencement of serious studies in the field of coordination chemistry. Thus Werner and Miolati [1] were able to use conductance data in aqueous solution in some of their earliest work on ammines. However, except for the simplest complexes of (usually) inorganic ligands, the use of water as a solvent for conductance purposes is often undesirable because of problems of hydrolysis, or is impracticable because of solubility difficulties. Accordingly the use of water for such studies has declined and the use of organic solvents has increased rapidly, particularly over the last twenty years. Unfortunately, the number of such solvents which have been used for studies of coordination compounds, the wide variation in the types of complexes studied, and the differences in experimental conditions used, has led to the present situation in which there is much confusion in relation to the conductance ranges to be expected for a particular electrolyte type. Even for the commonly used solvents such as acetone, a cursory examination of the literature reveals conflicting ranges of conductance data, the incorrect assignment of electrolyte type, and unjustified correlations with possible structures.

The present review therefore aims

(a) to attempt to rationalise the available data and to provide acceptable reference ranges for the most widely found electrolyte types in the common solvents,

(b) to identify any special effects common to particular types of complexes, ligands, or balancing ions;

(c) to emphasise the criteria for use of a particular solvent,

(d) to point out the aspects of the theories of conductance which need to be particularly considered in the design of experiments to obtain valid data for coordination compounds.

It is emphasised that the review is written for the purpose of providing basic data on coordination compounds, and not to develop or elaborate on conductance theory for such compounds Indeed, the present state of knowledge in this area does not allow of such treatment, and a detailed, comprehensive, and properly designed study of the conductance of coordination compounds in organic solvents should prove a profitable area of research.

In making this compilation of data, any values which appeared suspect, whether for experimental (e.g. solvolytic) or interpretational reasons, have been excluded. The interpretation of the data in terms of possible structures was not considered to be one of the purposes of the review, although it cannot be too strongly emphasised that conductance data in solution can only relate indirectly to structural problems associated with the complexes in the solid state.

## B SOLVENT CONSIDERATIONS

There are several standard texts available (e g. refs. 2,3) which, in considering most aspects of the use of non-aqueous solvents, include, inter alia, conductivity data (though not specifically relating to coordination compounds), and reference should be made to such texts for detailed information on solvent properties. A recent and valuable review of the conductivity of (mainly) the simpler electrolytes in non-aqueous solvents has been given by Barthel [4], and the development of a coordinating model for such solvents has been published [5].

For most purposes, the criteria most relevant to the selection of a solvent for conductivity determinations on complexes are its dielectric constant, viscosity, specific conductivity, ease of purification, and donor capacity towards metal ions Some generally accepted values of the first three of these parameters for the commonly used organic solvents are in Table 1.

TABLE 1

Some properties of non-aqueous solvents relevant to their use for conductivity measurements [a]

| *Solvent* | *Dielectric constant* | *Viscosity ($g^{-1}$ $sec^{-1}$)* | *Specific conductivity ($ohm^{-1}.cm^{-1}$)* |
|---|---|---|---|
| Acetone | 20.7[b] | 0 295[c] | 5 8 $\times 10^{-8}$ |
| Nitromethane | 35.9[b] | 0.595[c] | 6.56 $\times 10^{-7}$ |
| Nitrobenzene | 34 8[b] | 1.634[c] | 9.1 $\times 10^{-7}$ |
| Methanol | 32.6[b] | 0 545[b] | 1 5 $\times 10^{-9}$ |
| Ethanol | 24.3[b] | 1 078[b] | 1 35 $\times 10^{-9}$ |
| Acetonitrile | 36 2[b] | 0 325[c] | 5.9 $\times 10^{-8}$ |
| Dimethylformamide[d] | 36.7[b] | 0 796[b] | 0 6 – 2.0 $\times 10^{-7}$ |
| Dimethylsulphoxide | 46.6[b] | 1.960[b] | 3 0 $\times 10^{-8}$ |
| Pyridine | 12 3[b] | 0.829[c] | 4.0 $\times 10^{-8}$ |

[a] Abstracted from ref. 2. [b] 25°C. [c] 30°C. [d] Abstracted from ref. 325.

In qualitative terms, a solvent with a high dielectric constant and low viscosity will be preferred for conductivity purposes, and on this basis acetonitrile, nitromethane, and methanol may be selected as particularly useful. The use of both nitrobenzene and dimethylsulphoxide suffers from their high viscosity; there are, of course, other disadvantages, most notably the odour of nitrobenzene and the strong donor capacity of DMSO. Pyridine suffers from a low dielectric constant, unpleasant working effects, and strong donor properties; as a solvent for conductivity work on complexes it is effectively valueless, and will not be considered further.

The donor capacity of organic solvents towards metal ions and complexes has been studied by several methods, and has been reviewed recently [5-7]. In many cases solid adducts containing coordinated solvent have been isolated and studied, and details are given in the compilations for individual solvents. The coordination of solvent, whether or not it involves displacement of other ligands, need not prejudice the interpretation of the original complex provided it is recognised that such coordination has occurred, and that no change in electrolyte type has been caused. The latter condition will be satisfied in the replacement of a neutral ligand by a neutral solvent molecule, but it will break down in other cases such as displacement of (usually) an anionic ligand by a neutral solvent molecule, and solvolytic reactions involving displacement of a proton from the solvent. If a reaction involving a change of electrolyte type has occured, the extent of the reaction necessarily affects the calculated $\Lambda_M$ value, and normally renders its use impossible. A rough order (derived from heats of reaction) of the donor capacity of the common organic solvents for metal ions is dimethylsulphoxide > dimethylformamide > acetonitrile > nitromethane [7]. It should be emphasised that the latter two solvents are weaker donors than is water.

All the solvents considered in this review are available in a fairly high state of purity (> 99%), and acetone, ethanol, methanol, and nitrobenzene to better than this level. Details of subsequent purification procedures are in the standard texts, and are not repeated here. The main criteria for conductivity purposes are absence of water and dissolved gases, particularly oxygen (see, for example, ref. 8), and that the conductivity of the solvent should be reduced to the minimum practicable. References to useful variations of the standard methods of purification are given in the various parts of sections D – J of this review.

For acetonitrile, dimethylformamide, and dimethylsulphoxide, difficulties of purification relative to the other solvents might be considered to prejudice their use in conductivity work, but this could only be considered as a marginal matter

As an overall, though rather subjective, assessment it seems clear that nitromethane should be the preferred solvent for conductivity studies of coordination compounds. The subsequent order of preference is difficult to assess, nitrobenzene suffers from the rather low $\Lambda_M$ values, and its odour and high viscosity. Acetonitrile suffers mainly from the high donor capacity but in most other respects is satisfactory, whilst acetone, although apparently satisfactory in principle, has proved rather unreliable in practice (vide infra). Provided that care is taken to assess hydrolytic effects for methanol, and donor effects for dimethylformamide, both may continue to find some uses, but the remaining solvents would appear to be of little value.

## C EXPERIMENTAL CONSIDERATIONS

The commonly adopted procedure is to determine the specific conductivity, $\kappa$, of a solution by measuring the resistance, $R$, in an experimental cell of known cell constant, the cell forming one arm of a Wheatstone bridge circuit. Then $\kappa$ is calculated for the expression

$$\kappa = \text{cell constant}/R$$

The most widely used expressions for comparison of electrolytes are either the equivalent conductivity, $\Lambda_e$, or the molar conductivity, $\Lambda_M$, which are related to $\kappa$ by the expressions

$$\Lambda_e = \kappa V_e \quad \text{and} \quad \Lambda_M = \kappa V_M$$
$$\Lambda_e = \kappa / c_e \quad \text{and} \quad \Lambda_M = \kappa / c_M$$

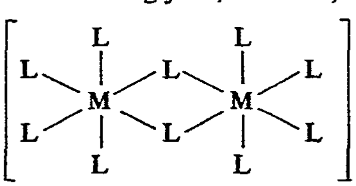
where $V_e$ and $V_M$ are the volumes (in $cm^3$) containing one equivalent or mole of solute respectively, and $c_e$ and $c_M$ are the concentrations of solute expressed in equiv $cm^{-3}$ or mole.$cm^{-3}$ respectively

In practice, the majority of workers have calculated $\Lambda_M$ values at a single concentration from an assumed molecular weight, and related the values to particular ranges supposed from previous work to represent a given electrolyte type. This method is open to several criticisms, notably

(i) that the single concentration is frequently chosen arbitrarily, and in many cases even for a series of related compounds is chosen differently, thus making direct comparison difficult;

(ii) that, as was pointed out by Hayter et al [9,10] and frequently emphasised subsequently (see, for example, ref. 11), the method requires the assumption of a molecular weight which may well be erroneous

The first point can be rectified, at least in principle, by the measurements always being made at the same concentration, but the second point can lead at worst to definite errors in interpretation and at best to confusion. This may be simply illustrated by considering a bivalent metal ion known to form octahedral complexes under normal conditions, which was found to give a complex of empirical formula $ML_5X_2$, where L is a ligand which is normally unidentate and X is a halide. Assuming that the spectral and magnetic properties supported the expected octahedral environment for $M^{II}$, it would be tempting to formulate the complex as the monomer $[ML_5X]X$, and to use a molecular weight calculated accordingly. If, however, the correct structure was the ligand-bridged dimer



$X_4$

then the molarity calculated on the basis of the monomer would be too high by a factor of 2, and the calculated $\Lambda_M$ would correspond to the range expected for a 2 1 electrolyte rather than either the correct 4·1 electrolyte or the incorrectly assumed 1.1 electrolyte This could well lead to the incorrect speculation that solvent interaction with the assumed 1:1 electrolyte had occurred

$$[ML_5X]X + S \rightarrow [ML_5S]X_2$$

It is probably true to say that this kind of speculative treatment of single-concentration conductivity data has been one of the main reasons for the distrust with which even carefully measured values have sometimes been received

By far the best method is to measure the conductivity over a concentration range governed by the solubility limit at one extreme and approach of the experimental values to that of pure solvent at the other This method not only allows more positive identification of dissociative effects and differences in electrolyte strength, but should allow application of the Onsager law.

$$\Lambda_0 - \Lambda_e = (A + \omega B \Lambda_0)\, c^{1/2}$$

The equivalent conductance $\Lambda_e$ is initially plotted against $c^{1/2}$ and the linear portion extrapolated to zero concentration to obtain $\Lambda_0$ as intercept. The factor $(\Lambda_0 - \Lambda_e)$ is then plotted against $c^{1/2}$ to obtain a straight line of slope $(A + \omega B \Lambda_0)$. Since the term $(A + \omega B \Lambda_0)$ depends, amongst other factors, on the charges of the ions concerned, it will necessarily reflect directly the electrolyte type for the complex concerned The value of the method is well explained by Feltham and Hayter [9] who point out that since for complexes $[ML_4]X_2$ and $[M_2L_8]X_4$ the equivalent weight is in both cases half the *monomer* weight, a single $\Lambda_e$ determination cannot unambiguously determine either the molecular complexity $z$ in complexes $[ML_n]_z X_{yz}$, or the charge type However, the difference between the 2:1 and 4 1 electrolytes will be immediately obvious from the plots derived from the Onsager law. This derivation assumes that the anions X do not enter the coordination sphere. However, suppose the true complex in this case was $[ML_4X]X$ instead of an assumed $[ML_4]X_2$ Then the calculated equivalent concentration would be *twice* the true equivalent concentration, and the calculated $\Lambda_e$ values half the true values Hence, the calculated values of the ordinates $(\Lambda_0 - \Lambda_e)$ in the Onsager plot would be half the correct values and the calculated values of the abscissae $c^{1/2}$ would be $2^{1/2}$ too large. The calculated slope of the Onsager plot would hence be $1/2(2^{1/2})$ *less* than the value for a 1 1 electrolyte, and it would be hard to escape the conclusion that the initial postulate of a 2:1 electrolyte was wrong

Since the term $\omega$ involves, inter alia, ionic mobilities, which necessarily differ for the various complex ions, and since reliable $\Lambda_e - c^{1/2}$ plots are still uncommon for complexes, no attempt has been made to compile values for $(A + \omega B \Lambda_0)$ for various solvents and complexes, although in later sections reference is normally made to such $\Lambda_e - c^{1/2}$ studies.

It follows that for all conductivity measurements, whether over a concentration range or not, comparisons of the data are most valid for systems in which a series of complex cations are balanced by the same (non-complex) anions, or for the same cation balancing a series of complex anions. In particular, systems in which a complex cation is balanced by tetraphenylborate will have much lower $\Lambda_M$ values than for the analogous halides, since the ionic mobilities of the latter are so much greater than for tetraphenylborate. This can reach the point where a complex $[ML_n]\{(C_6H_5)_4B\}_2$ has $\Lambda_M$ reduced to the range typical of 1:1 electrolytes This point is fully illustrated in the following sections

## D NITROMETHANE

### *(i) General considerations*

Nitromethane has become the most widely used solvent for the determination of the molar conductivity of coordination compounds, and data are available for over 1,200 compounds Satisfactory reference values may be calculated from these data for all common electrolyte types, and since nitromethane possesses a number of advantages over other solvents, particularly nitrobenzene, its use may be expected to increase These advantages include the relatively high conductivity values obtained for a given electrolyte type (ca three times those for nitrobenzene), easier purification, absence of unpleasant working effects (e.g. odour, compare nitrobenzene), and the relatively low donor capacity Thus, although there has been a report [12] of the isolation of a solid adduct of nitromethane, formulated as non-conducting $TiCl_4$ $CH_3NO_2$, interpretational problems arising through dissociation caused by coordination of nitromethane seem to have been less than with, for example, acetonitrile. A recent example of dissociation in this solvent, but without coordination of the solvent, is the reaction

$$[Co(pyridine)_4Cl_2]\,(octahedral) \rightleftharpoons [Co(pyridine)_2Cl_2] + 2\ pyridine$$

which was shown kinetically to be very rapid [13].

Detailed methods for the purification of nitromethane are in the standard texts, methods employed for solvent intended specifically for conductivity work are given by Coetzee and Cunningham [14], Buffagni and Dunn [15], and Unni et al [16] A convenient method for obtaining pure nitromethane for general electrochemical work is described by Headridge [7] A frequently adopted method (see, for example, ref 17) is to dry "Specpure" nitromethane over molecular sieves or calcium sulphate, followed by careful fractionation For most purposes a conductivity of $\sim 2 \times 10^{-6}$ ohm$^{-1}$. cm$^{-1}$ is adequate, though for the more exacting reference work [14,16] values as low as $10^{-8} - 10^{-9}$ ohm$^{-1}$ cm$^{-1}$ are claimed.

Reference values for non-complex electrolytes are in Table 2, and lead to an average $\Lambda_M$ value for 1:1 electrolytes of $\sim$ 91.5 ohm$^{-1}$. cm$^2$ mole$^{-1}$. However, the values for the tetraphenylborate and tetraisoamyl borate salts are very low because of the low anionic mobilities noted earlier, and if these values are excluded from the overall average a value of $\sim$ 96 ohm$^{-1}$. cm$^2$ mole$^{-1}$ is obtained Average values for complexes of unidentate ligands (Table 3) are, for 1:1 electrolytes 88 5 ohm$^{-1}$ cm$^2$. mole$^{-1}$, and for 2:1 electrolytes 167 ohm$^{-1}$. cm$^2$ mole$^{-1}$. For the whole range of complexes which has been studied, values claimed for 1 1 electrolytes range from 60 to 115 ohm$^{-1}$. cm$^2$. mole$^{-1}$, with an average value of $\sim$ 83 ohm$^{-1}$. cm$^2$. mole$^{-1}$. For 2:1 electrolytes, values claimed cover the range 115–250 ohm$^{-1}$. cm$^2$. mole$^{-1}$, an average value being 168 ohm$^{-1}$ cm$^2$. mole$^{-1}$. Values as low as 180 and as high as 300 ohm$^{-1}$. cm$^2$. mole$^{-1}$ have been given for 3 1 electrolytes, a reasonable average value is 242 ohm$^{-1}$ cm$^2$. mole$^{-1}$ Contrary to a recent claim [47] of no precedent for measurements on 4:1 electrolytes, data have been given for at least ten such compounds covering a range 244 – 341 ohm$^{-1}$. cm$^2$ mole$^{-1}$, with an average value of 307 ohm$^{-1}$. cm$^2$. mole$^{-1}$ A very good example for this electro-

TABLE 2

Molar conductivity in nitromethane of selected non-complex compounds. Concentration $10^{-3}$ *M* except where otherwise specified.

| *Compound* | $\Lambda_M$ *(ohm$^{-1}$ cm$^2$ mole$^{-1}$)* | *Ref* |
|---|---|---|
| $[(CH_3)_4N]Cl$ | 106 8 | 16 |
| $[(CH_3)_4N]Br$ | 107 5 | 16 |
| $[(CH_3)_4N]I$ | 118.0 | 18 |
| $[(C_2H_5)_4N]Cl$ | 103 2 | 16 |
| $[(C_2H_5)_4N]Br$ | 127 0 [a] | 19 |
| $[(C_2H_5)_4N]Br$ | 103 0 | 20 |
| $[(C_2H_5)_4N]Br$ | 103 5 | 16 |
| $[(C_2H_5)_4N]I$ | 97 0 [b] | 21 |
| $[(C_2H_5)_4N]ClO_4$ | 104 0 | 22 |
| $[(n\text{-}C_3H_7)_4N]Cl$ | 95 2 | 16 |
| $[(n\text{-}C_3H_7)_4N]Br$ | 95 7 | 16 |
| $[(n\text{-}C_4H_9)_4N]Cl$ | 90 4 | 16 |
| $[(n\text{-}C_4H_9)_4N]Br$ | 90 8 | 16 |
| $[(n\text{-}C_4H_9)_4N]Br$ | 90 4 | 14 |
| $[(n\text{-}C_4H_9)_4N]Br$ | 79 0 | 23 |
| $[(n\text{-}C_4H_9)_4N](C_6H_5)_4B$ | 61 9 | 14 |
| $[(n\text{-}C_4H_9)_4N]NO_3$ | 82 0 | 23 |
| $[(i\text{-}C_5H_{11})_4N](C_6H_5)_4B$ | 59 4 | 14 |
| $[(i\text{-}C_5H_{11})_4N](i\text{-}C_5H_{11})_4B$ | 59 2 | 14 |
| $[(C_6H_5)_4P]NO_3$ | 80 4 [c] | 24 |
| $[(C_6H_5)_3CH_3As]I$ | 85 0 [b] | 21 |
| $[(C_6H_5)_4P][H(NO_3)_2]$ | 74 8 [d] | 24 |
| $[(C_6H_5)_4As][H(NO_3)_2]$ | 86 8 | 24 |
| $[TDPS\ CH_3]I$ [e] | 94 5 | 25 |
| $[(C_6H_5)_4As]_2(S_2C_2N_2)$ | 202 0 | 26 |

[a] $0.05 \times 10^{-3}$ *M* [b] $0 5 \times 10^{-3}$ *M* [c] $1 52 \times 10^{-3}$ *M* [d] $2 5 \times 10^{-3}$ *M*. [e] TDPS = tris(dimethylamino) phosphine sulphide, $[(CH_3)_2N]_3PS$.

lyte type, and for the careful use of conductivity measurements generally, is the paper of Bagnall and co-workers [48], data for the other 4.1 electrolytes are in refs 49 – 53. An unusual electrolyte type is the compound $[CrL_3]_2(SO_4)_3$, where L = 2-aminomethylpyridine, for which a value of $\Lambda_M$ = 419 ohm$^{-1}$ cm$^2$. mole$^{-1}$ is quoted [54]

TABLE 3

Molar conductivity in nitromethane of selected compounds containing a complex anion and a non-complex cation Concentration $10^{-3}M$ except where otherwise specified.

| *System* | *Range* $\Lambda_M$ | *No of values* | *Average* $\Lambda_M$ | *Comments* | *Ref* |
|---|---|---|---|---|---|
| $A^+[ReOX_4]$ | 83.5–114 | 3 | 96.8 | A = $(C_6H_5)_4As$, $(n\text{-}C_4H_9)_4N$, X = Cl, Br | 27 |
| $A^+[MoOX_4]$ | 65–69.3 | 3 | 67.8 | A = $(C_6H_5)_4As$, quinolinium, X = Cl, Br | 28 |
| $A^+[SiF_5]$<br>$A^+[BF_4]$ | 87–108 | 6 | 97.3 | A = $(C_2H_5)_4N$, $(n\text{-}C_3H_7)_4N$, $(C_6H_5)_4As$ | 29 |
| $A^+[AuX_4]$ | 87.5–96 | 3 | 91.1 | A = $(C_2H_5)_4N$, bipyH, X = Cl, Br | 30 |
| $(C_2H_5)_4N[Al(NO_3)_4]$ | 60.5–125 | 1 | 98.2 | Over conc range, average at $10^{-3}$ *M* | 31 |
| $A^+[Fe(NO_3)_4]$ | 76–82 | 4 | 80.0 | A = $(C_2H_5)_4N$, $(C_2H_5)_3NH$, $(C_2H_5)_2NH_2$, $(C_2H_5)NH$ | 32, 33 |
| $[A^+]_2[CoX_4]$ | 153–183 [c] | 4 | 1/1.0 [c] | A = $(C_6H_5)_4As$, $(C_2H_5)_4N$, X = NCS, NCSe | 34 |
| $[(C_6H_5)_4As]_2[Ni(NCO)_4]$ | 215 | 1 | 215.0 [a] | | 35 |
| $[A^+]_2[MX_4]$ | 151–200 | 15 | 173.3 [b] | A = $(C_2H_5)_4N$, $(C_6H_5)_3CH_3As$, M = Ni, Co, Mn, Zn, Cu, X = Cl, Br, I | 21 |
| $[(C_6H_5)_3(n\text{-}C_4H_9)P]_2[UX_6]$ | 115–127 | 3 | 121.3 | X = Cl, Br | 374 |
| $[(C_6H_5)_4As]_2[ReBr_6]$ | 146 | 1 | 146.0 | | 36 |
| $[A^+]_2[NiX_4]$ | 158, 168 | 2 | 163.0 | A = $(C_6H_5)_3CH_3P$, $n\text{-}(C_4H_9)_4N$, X = Cl, I | 375 |
| $[(C_6H_5)_4P]_2[UX_6]$ | 163–165 | 3 | 164.3 | X = Cl, Br | 37 |
| $[A^{2+}][NiI_4]$ | 160 | 1 | 160.0 | A = complex phosphetanium cation | 38 |
| $[A^+]_2[MX_4]$ | 180, 200 | 2 | 190.0 | A = $(C_2H_5)_4N$, pyridinium, picolinium, L = pyridine, α-picoline, X = Cl, Br, I, M = Co, Ni, Zn | |
| $[A^+][MLX_3]$ | 78–114 | 16 | 94.0 | | 39 |
| $[(CH_3)_4N]_2[SiF_6]$ | 149 | 1 | 149.0 | | 29 |
| $[A^+]_2[Pt(NCO)_4]$ | 214, 251 | 2 | 232.5 | A = $(C_2H_5)_4N$, $(C_6H_5)_4As$ | 40 |

TABLE 3 (continued)

| *System* | *Range* $\Lambda_M$ | *No of values* | *Average* $\Lambda_M$ | *Comments* | *Ref.* |
|---|---|---|---|---|---|
| $[(C_2H_5)_4N][NiLBr_3]$ | 106 | 1 | 106.0 | L = benzimidazole | 41 |
| $[(n\text{-}C_4H_9)_4N][Mo(CO)_3I_3\ P(C_6H_5)_3]$ | 93.3 | 1 | 93.3 | | 42 |
| $[A^+][NiP(C_6H_5)_3X_3]$ | 71.6, 79.8 | 2 | 75.7 | A = $(C_2H_5)_4N$, $(n\text{-}C_4H_9)_4N$, X = Br, I | 43 |
| $[A^+][CoP(C_6H_5)_3X_3]$ | 72.0, 85.0 | 2 | 78.5 | A = $(C_2H_5)_4N$, $(n\text{-}C_4H_9)_4N$, X = Cl, Br | 44 |
| $[A^+][Rh(CO)_2I_4]$<br>$[A^+][Rh(CO)LI_4]$ | 70.0 – 80.0 | 4 | 77.3 | A = $(C_2H_5)_4N$, $(C_6H_5)_4As$; L = pyridine, aniline | 45 |
| $[(CH_3)_4N][RuCl_2(SnCl_3)_2]$ | 113.0 | 1 | 113.0 | | 46 |
| $[(C_6H_5)_3PH][RuCl_2(SnCl_3)_2]$ | 87.0 | 1 | 87.0 | | 46 |
| $[(CH_3)_4N]_2[RhCl(CO)(SnCl_3)_2]$ | 135.0 | 1 | 135.0 | | 46 |
| $[(CH_3)_4N]_2[PtCl_2(SnCl_3)_2]$ | 128.0 | 1 | 128.0 | | 46 |
| $[A^+]_4[Ir_2Cl_6(SnCl_3)_4]$ | 162.0, 244.0 | 2 | 203.0[c] | A = $(CH_3)_4N$, $(C_6H_5)_3PH$ | 46 |

[a] $2.49 \times 10^{-3}$ *M* [b] $0.5 \times 10^{-3}$ *M* [c] Over concentration range, value interpolated at $10^{-3}$ *M*

In summary, acceptable ranges for complexes of the various electrolyte types at concentrations ca. $10^{-3}$ $M$ are suggested as. 1:1, 75 – 95; 2:1, 150 – 180, 3:1, 220 – 260; 4:1, 290 – 330 $ohm^{-1}.cm^{2}.mole^{-1}$. Values significantly outside these ranges should be interpreted with caution

*(ii) Nitrogen donors*

There have been approximately 100 papers containing conductivity measurements on complexes of nitrogen donors in nitromethane The data are not easy to correlate, mainly because the wide variety of ligand systems investigated leads to complexes which, although in many cases of comparable stereochemistry, are quite different in their stability and behaviour in solvents

For simple complexes $R_2[MX_4]$ (R = $(C_2H_5)_4N$, $(C_6H_5)_4As$, M = Co, Ni, Pt, X = NCS, NCSe, NCO) the most comprehensive set of data [34] agrees well with the suggested ranges for 2 1 electrolytes It is difficult to rationalise the other data [35,40] since the values given (214, 215, 251 $ohm^{-1}$ $cm^{2}.mole^{-1}$) lie in the range for 3 1 electrolytes Most of the other unidentate ligands studied concern pyridine and its derivatives, Rosenthal and Drago [55] have studied some nickel(II) pyridine complexes, including the effects of added ligand, and Greenwood et al [8] have made a careful study of, for example, $WCl_5$(pyridine)$_2$, which is formulated as [$WCl_4$(pyridine)$_2$] Cl on the basis of $\Lambda_M$ = 85 $ohm^{-1}.cm^{2}.mole^{-1}$ A rather unusual example concerns the $Co^{II}$, $Ni^{II}$, and $Cu^{II}$ complexes of 2-cyanopyridine, for which reaction with the alcohol used in the preparation leads to complexes of different ligands [56]. Tetramethylguanidine appears to function as a unidentate ligand through one N only, giving [57] complexes $[ML_4](ClO_4)_2$.

Bidentate nitrogen donors cover a range of familiar ligands, notably the heterocyclic systems such as bipyridyl and *o*-phenanthroline, and the aliphatic amines based on, for example, ethylenediamine. Some of the most interesting results for the first type of ligand are found for Ga[58] and In[59], and for transition elements in their lower valence states [60,61]. Thus, complexes $InCl_3L_{1.5}$, which do not obey the Onsager law, are formulated [59] as ionic dimers $[InCl_2L_2][InCl_4L]$, with subsequent dissociation according to

$$[InCl_2L_2]^{+} + CH_3NO_2 \rightleftharpoons [InClL_2.CH_3NO_2]^{2+} + Cl^{-}$$

Even so, $\Lambda_M$ is only ~ 2/3 of the expected value for a 1 1 electrolyte; similar problems arise for $Mo^{II}$, $Mo^{III}$, and $V^{III}$. Harris and Mackenzie [62,63] have published data for $Ni^{II}$ complexes of bipyridyl and *o*-phenanthroline, and used $\Lambda_M$ values of 34 and 36 $ohm^{-1}.cm^{2}.mole^{-1}$ in nitrobenzene, and 173 and 170 $ohm^{-1}.cm^{2}.mole^{-1}$ in nitromethane for $NiL_2(ClO_4)_2.nH_2O$ ($n$ = 2,3) to support, rather optimistically, $ClO_4^-$ coordination in the former solvent but not the latter. For further conductivity data on complexes of these ligands see, for example, refs. 64–67 and 30. The conductivity of complexes of 2,9-dimethyl-*o*-phenanthroline [68], 4,6,4′,6′-tetramethyl-2,2′-bipyridyl [22,69], and terpyridyl [70–72] follow established patterns. Sutton and his co-workers have published a considerable amount of conductivity data for complexes of bidentate heterocyclic donors, and refs. 17, 73–76 and 345 are only a representative sample of this valuable work. The most typical data for complexes of ethylenediamine are provided by the work of Meek [77,78].

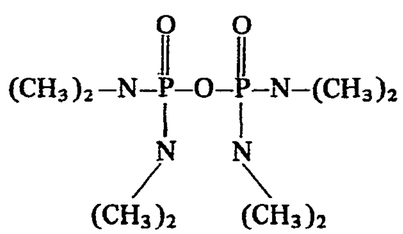
For polydentate N donors the most important conductivity data are found for systems in which a ligand with an invariant number of donor sites reacts with a series of metal salts to give complexes of comparable geometry and electrolyte type. Good examples are the five-coordinate complexes [MLX] X where M = Mn, Fe, Zn, X = Br, I, L = tris(2-dimethyl-aminoethyl)amine [79], and the seven coordinate complexes $[FeLX_2]X'$ where $X = X'$ = two from Cl, Br, I, NCS, $ClO_4$, $BF_4$, and L is a polydentate ligand. More commonly, however, the complexes formed by such ligands vary in their stereochemistry and electrolyte type, and the problems of using conductivity data to assist in structural determinations are considerable. The problems encountered by McWhinnie et al. [80–82] with complexes of tri-(2-pyridylamine) are typical, and a particularly good example of the interpretational problems where $\Lambda_M$ is significant but not fully characteristic of a 1·1 electrolyte is the work of Nelson et al [83,84]. This work also provides a good example of the differences in anion coordination in solution, thus $[NiL(ClO_4)[ClO_4$ and $[NiL(NO_3)]ClO_4$ have $\Lambda_M$ = 160 and 93 $ohm^{-1} . cm^2 \ mole^{-1}$, the coordinated $ClO_4^-$ presumably being dissociated in solution in the first case Complexes of heterocyclic substituted ethylenediamines [50,85] pyrazines and triazines [86] provide other useful sources of $\Lambda_M$ data

*(iii) Oxygen donors*

Conductivity data for complexes of oxygen donors are extensive, and arise largely through studies of lactams, phosphoramides, and tertiary *N*- and *P*-oxides.

Complexes of a variety of lactams have been particularly studied by Madan et al [87–89], and in general provide a valuable source of $\Lambda_M$ data However. there are several rather worrying anomalies, thus, complexes of the formula $[ML_6](ClO_4)_3$, where L = $\gamma$-butyrolactam, are found [87] to have $\Lambda_M$ = 215 and 222 $ohm^{-1} \ cm^2 . mole^{-1}$, whereas $[CoL_4](ClO_4)_2$ (L = *N,N*-dimethylthioacetamide) is reported by the same author [90] as having $\Lambda_M$ = 220 $ohm^{-1} \ cm^2 \ mole^{-1}$. Even within the same paper [88], on $\epsilon$-caprolactam complexes, $[CrL_6](ClO_4)_3$ is reported as $\Lambda_M$ = 212 8 and $[FeL_6](ClO_4)_2$ as 193 5 $ohm^{-1} . cm^2 \ mole^{-1}$, respectively For further papers on lactam complexes see refs 91 and 92

Complexes of octamethylpyrophosphoramide(I) have been studied in detail by Joesten et al. [51,93–95], and of hexamethylphosphoramide by Donoghue et al [96–98]



(I)

These papers contain data for some 60 complexes, including 4 1 electrolytes [51,53]. Complexes of a similar type are those of the substituted phosphonates [99,100]. Substituted amide ligands in which coordination is through either one [101] or two [102,103] carbonyl groups have been studied, as have the closely related complexes of 1,3-dimethylurea [104], and substituted acetanilides [105]

The heterocyclic *N*-oxides have proved fruitful ligand systems, and some typical conductivity data for complexes of this type of ligand are in refs. 106–108. A good example of the careful use of $\Lambda_M$ data, including a study of concentration and added ligand effects, is in ref 109. The abnormally high values for the lanthanide 2,2-bipyridyl-*N*-oxide complexes $[LnL_4](ClO_4)_3$ should also be noted [110]

Of the simpler O-donors, the β-diketones are perhaps best known, and $\Lambda_M$ data for complexes of this class of ligand have been reported [111,112] However, the most important examples for simple O-donors concern the use of conductivity measurements to support the existence of complexes containing the $[Fe(NO_3)_4]^-$ and $[Al(NO_3)_4]^-$ ions [31–33]. For both systems, concentration–conductivity data are given and interpreted, the behaviour for the iron system in particular being far from ideal

*(iv) Phosphorus donors*

The investigation of complexes of simple phosphorus donor molecules, whether uni- or polydentate, have not produced any highly unusual conductivity results, typical examples being refs. 8, 43, and 113 A rather interesting complex is $[RuCl(CS_2)\{P(C_6H_5)_3\}_3]Cl$, investigated by Wilkinson et al. [114], the investigation by Carty [115] of complexes of the type $GaX_3L$, formulated as $[GaL_2X_2][GaX_4]$, also provides some interesting results. An unusual ligand system is the cyclic cationic system 3-[(diphenylphosphino)methyl]-3-methyl-1,1-diphenylphosphetanium chloride investigated by Berglund and Meek [38]. Complexes of mixed P–S, P–As, and P–Se donors have been investigated, particularly by Meek et al [116–121], and these systems, chiefly [MLX]X′ where L is a quadridentate donor, X = halide, pseudohalide, and $X' = ClO_4^-$, $B(C_6H_5)_4^-$ etc , provide valuable data for 1·1 electrolytes However, the most detailed and important paper is that by Westland and Pluščec [122], who describe a careful concentration–conductivity study for a series of $Pt^{II}$ and $Pd^{II}$ complexes $[ML_2]X_2$, where L = 1,3-di(phenylthio) propane, 1,2-bisdiphenylphosphinoethane, and 1,2-di(phenylthio)ethane, and $X = ClO_4^-$, $BF_4^-$, and $PF_6^-$. Anionic effects, the effects of added ligand, and the various possible equilibria are considered, and it is noted that in this case the Pt complexes are weaker electrolytes than the Pd complexes

*(v) Arsenic donors*

Most of the data under this heading derive from the diarsine type of ligand, typical of the earlier papers are those of Nyholm and co-workers [123,124], and more recently there has been a report [125] of data for complexes formulated as $[Fe(diars)_2X_2](X')_2$, apparently containing $Fe^{IV}$ The current discussions of the electronic structure of such systems is unlikely to require reinterpretation of the conductivity data. For other arsine type ligands see ref 126, and the section on carbonyl and nitrosyl complexes (refs 127, 128). Complexes of mixed As–P and As–N donors also provide useful data, chiefly for 1 1 electrolytes [116,117,129,130].

*(vi) Carbonyls, nitrosyls, and cyclopentadienyls*

There have been several investigations of complexes with CO as ligand, usually in conjunction with other (unidentate) ligands. Good examples are the investigations of Ruff [131,132] on halogen-bridged and simple binuclear carbonyl anion systems, of Nyholm and co-workers [133], and of Kingston and Scollary [45] Perhaps the most interesting systems examined [128] are those containing the $\mu$-(dimethylarsenido)- and dimethylphosphido-di-$\pi$-cyclopentadienyltetracarbonyldiiron cations, with $ClO_4^-$ and $(C_6H_5)_4B^-$ anions The value for the perchlorate is a little high, perhaps indicating some dissociation of the cation, but the data for the tetraphenylborates are typical of systems with this anion

The solitary investigation [127] of nitrosyl complexes is nevertheless of considerable interest since it contains detailed $\Lambda_M$—concentration plots and a careful interpretation of the data.

The most consistent conductivity data for $\pi$-cyclopentadienyl complexes are given by Green and co-workers [134–136] and by Locke and McCleverty [137]

*(vii) Sulphur donors*

Studies of unidentate sulphur donors have been limited to derivatives of thiourea [138,139], 1,4-thioxane [140], and 2-thiazolidenethione [141] For bidentate sulphur donors there is now available a considerable body of conductivity information, largely resulting from the current interest in dithiolate complexes The great value of these complexes from a conductivity point of view is that they yield many systems of the same electrolyte type in which the anionic complex is balanced by a series of non-complex (often quaternary ammonium, phosphonium, or arsonium) cations Thus data are available for some 80 complexes of comparable electrolyte type. Typical data are in refs 142–146.

Data for complexes of some macrocyclic sulphur donors are given by Rosen and Busch [47], and include values for 4:1 electrolytes. Data are also available for the rather unusual complexes of some mercaptoboranes [147]

Complexes of mixed S—N ligands have been particularly widely investigated by Livingstone and co-workers (see, for example, refs 148, 149), and by Sutton (see, for example, refs. 150, 151). Complexes of di-(2-pyridyl)sulphide and of quinoxaline-2,3-dithiol have been the subject of recent studies [152,153], and complexes of mixed S—P and Se—P ligands have also been investigated [118–121,154]. In all cases the conductivity data are in satisfactory agreement with the suggested ranges.

*(viii) Lanthanide complexes*

Data for complexes of the lanthanides are normally most valuable as a source of information for 3.1 electrolytes However, the information available for complexes in nitromethane is confusing; one set of data [91] for some 13 complexes of *N*-methyl-$\gamma$-butyrolactam yields an average $\Lambda_M$ of ~ 222 ohm$^{-1}$ cm$^2$. mole$^{-1}$ at $c = 2 \times 10^{-3}$ *M*, whilst for other butyrolactam complexes an average value at $c = 10^{-3}$ *M* is ~ 290 ohm$^{-1}$. cm$^2$. mole$^{-1}$, and at $3 \times 10^{-3}$ *M* is ~ 232 and 286 ohm$^{-1}$ cm$^2$. mole$^{-1}$ respectively, depending on the ligand [89]. Even more surprisingly, at $c = 10^{-3}$ *M* a series of complexes [110] of 2,2-bipyridyl-*N,N*-dioxide have $\Lambda_M$ (average) ~ 394 $ohm^{-1}$. $cm^2$. $mole^{-1}$, and at 5 X $10^{-3}$ *M*, ~ 282 $ohm^{-1}$. $cm^2$. $mole^{-1}$. These values are approaching the range independently measured by several sets of workers (section D (i)) for 4:1 electrolytes and may perhaps be due to impure solvent.

*(ix) Miscellaneous complexes*

An interesting series of complexes of 2:1, 3.1, and 4 1 electrolyte types containing the $Nb_6Cl_{12}$ cluster has been investigated [52], the $\Lambda_M$ data fit very satisfactorily with values for other simpler systems. Recently, Greenwood and Sharrocks [155] have prepared complexes of the general formula R[$CoX_2$(pyridine)$_2$(decaborane)], where R = tetraalkylammonium, X = Cl, Br, other unusual complexes are those of *p*-methoxyphenylisocyanide [156]

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*(i) General considerations*

There have been some 150 papers published which contain significant conductivity data for complexes in nitrobenzene, with a total of conducting compounds studied approaching 900. In many other cases the absence of significant conductivity has also been used diagnostically In order to rationalise these data, and to avoid the difficulties of comparing values for systems of widely differing structures, the main tabulation is for systems containing non-complex cations and complex anions of unidentate ligands. Since, for most of the systems, the ligand is a halide or a pseudohalide, these are tabulated separately by electrolyte type (Tables 4–6) Values for other complexes of unidentate ligands are in Table 7, and some reference values are in Table 8 The data in the latter table are not intended to supersede the compilations already available in the standard texts, but rather to indicate values which have been obtained under identical conditions to those used for complexes. For 1 1 electrolytes an average value of $\Lambda_M$ = 27 $ohm^{-1}$ $cm^2$ $mole^{-1}$ is obtained, though the figure is rather higher (ca. 30 $ohm^{-1}$. $cm^2$ $mole^{-1}$) for the non-complex compounds If an average value is taken for all uniunivalent complex compounds which have been measured, ignoring concentration effects, and omitting only those values which seem irreconcilable with the majority of values, a value of ca. 25 $ohm^{-1}$. $cm^2$. $mole^{-1}$ is obtained The main reasons for this lower value would seem to be solvent interactions and the low ionic mobilities of some of the ions involved. For 2 1 electrolytes, average values are 55 $ohm^{-1}$. $cm^2$. $mole^{-1}$ (tabulated data), and 52 5 $ohm^{-1}$. $cm^2$. $mole^{-1}$ (all complexes). The corresponding values for 3:1 electrolytes are 73 and 78 $ohm^{-1}$. $cm^2$. $mole^{-1}$, respectively, and for 4·1 electrolytes 95 $ohm^{-1}$ $cm^2$. $mole^{-1}$ (tabulated values only). As working ranges for complex compounds at ca. $10^{-3}$ *M* the following therefore seem reasonable 1:1, 20–30; 2:1, 50–60; 3:1, 70–82, 4.1, 90–100 $ohm^{-1}$. $cm^2$. $mole^{-1}$. In special cases, particularly those complexes containing the tetraphenylborate anion, values below these limits may be accepted.

TABLE 4

Molar conductivity in nitrobenzene of 1 1 electrolytes containing an uncomplexed cation and a complex anion of halide or pseudohalide ligands

| *Complex* | $\Lambda_M$ | $c \times 10^3$ | *Ref* |
|---|---|---|---|
| $[A]^+[BCl_4]$ | 26 0[a] | 1 0 | 157 |
| $[A]^+[AlCl_4]$ | 24 0[a] | 1.0 | 157 |
| $[A]^+[SbCl_6]$ | 27 0[a] | 1 0 | 157 |
| $[A]^+[SbCl_6]$ | 22.0[b] | 1.0 | 157 |
| $[(C_6H_5)_3CH_3As]^+[TlCl_4]$ | 25 1 | 7 4 | 158 |
| $[(C_6H_5)_3CH_3As]^+[TlBr_4]$ | 26.4 | 6 0 | 158 |
| $[(C_6H_5)_3CH_3As]^+[TlI_4]$ | 24.8 | 5 1 | 158 |
| $[(n\text{-}C_4H_9)_4N][BF_4]$ | 31 0[c] | 1 0 | 159 |
| $NH_4[Ti(SCN)_4]$ | 18 9 | 3 0 | 160 |
| $[(C_2H_5)_2N][AuBr_4]$ | 32.8 | 1.0 | 30 |
| [Bipyridyl H] $[AuCl_4]$ | 31 1 | 1 0 | 30 |
| [Bipyridyl H] $[AuBr_4]$ | 30 8 | 1 0 | 30 |

[a] Cation is $\{(C_6H_5)_2C = N = C(C_6H_5)_2\}^+$. [b] Cation is $\{(p\text{-tolyl})_2C = N = C(C_6H_5)_2\}^+$ [c] Value calculated from Λ, *c* data given

The value of conductivity—concentration plots has been emphasised in the general introduction to the review, and there have been several important examples of this approach for nitrobenzene. Thus, Beurskens and co-workers [170] give data and a careful interpretation for the compound bis(*N,N*-di-n-butyldithiocarbamato)gold(III) dibromoaurate(I). Hawkes and Ginsberg [179] have interpreted data for compounds of the general formula $[(C_2H_5)_4N]_2[Re(CO)_3X_3]$, a valuable early paper covering all electrolyte types except 4.1 is that of Martin and Waind [180] on some complexes of bipyridyl Other examples of $\Lambda_M - c^{1/2}$ data for complexes are in refs 111 and 181, and a recent and important paper on non-complex compounds is that of Barreira and Hills [182]. The earliest significant paper for complexes, by Foss and Gibson [183], contains data at several concentrations, and it is regrettable that this example has only rarely been followed. A good review of the precautions necessary for conductivity determinations in nitrobenzene is given by Greenwood and co-workers [8].

Finally, it may be noted that useful examples of methods of purification of nitrobenzene for conductance work are in refs 17, 175, and 182, although many authors have suggested variations on these and other standard methods

### *(ii) Oxygen donors*

Complexes of oxygen donors may conveniently be surveyed under the headings of unidentate donors, the ligands being nitrogen, arsenic, and sulphur oxides, and of chelating ligands such as β-diketones

TABLE 5

*Molar conductivity in nitrobenzene of 2 1 electrolytes containing an uncomplexed cation and a complex anion of halide and pseudohalide ligands*

| *Complex* | $\Lambda_M$ | $c \times 10^3$ | *Ref* |
|---|---|---|---|
| $[(CH_3)_4N]_2[Co(NCS)_4]$ | 62 6 | 1 0 | 161 |
| $K_2[Co(NCS)_4]$ | 63 0 | 1 0 | 161 |
| $[(CH_3)_4N]_2[Co(NCSe)_4]$ | 61 0 | 1 0 | 162 |
| $[(C_6H_5)_4As]_2[Co(NCSe)_4]$ | 43 0 | 1.0 | 162 |
| $[(C_6H_5)_4As]_2[Co(NCSe)_4]$ | 54 0 | 0 21 | 34 |
| $[(C_6H_5)_4As]_2[Co(NCSe)_4]$ | 50 0 | 0 54 | 34 |
| $[(C_6H_5)_4As]_2[Co(NCSe)_4]$ | 47.0 (46 7) [a] | 0 96 | 34 |
| $[(C_2H_5)_4N]_2[Co(NCSe)_4]$ | 64 0 | 0 26 | 34 |
| $[(C_2H_5)_4N]_2[Co(NCSe)_4]$ | 58 0 | 0 54 | 34 |
| $[(C_2H_5)_4N]_2[Co(NCSe)_4]$ | 57 0 (56 8) [a] | 0 94 | 34 |
| $[(C_6H_5)_4As]_2[Co(NCS)_4]$ | 53 0 | 0 25 | 34 |
| $[(C_6H_5)_4As]_2[Co(NCS)_4]$ | 50 0 | 0 55 | 34 |
| $[(C_6H_5)_4As]_3[Co(NCS)_4]$ | 48 0 (47 7) [a] | 0 96 | 34 |
| $[(C_2H_5)_4N]_2[Co(NCS)_4]$ | 65 0 | 0 26 | 34 |
| $[(C_2H_5)_4N]_2[Co(NCS)_4]$ | 56 0 | 0 55 | 34 |
| $[(C_2H_5)_4N]_2[Co(NCS)_4]$ | 54 0 (53 4) [a] | 0 88 | 34 |
| $[(C_2H_5)_4N]_2[Co(NCS)_4]$ | 55 4 | 1 0 | 163 |
| $[(C_2H_5)_4N]_2[CoBr_4]$ | 48 7 | 1 0 | 163 |
| $[(C_2H_5)_4N]_2[CoI_4]$ | 54.2 | 1 0 | 163 |
| $[(C_2H_5)_4N]_2[Co(NCS)_4]$ | 59 0 | 1.0 | 164 |
| $[(C_2H_5)_4N]_2[Mn(NCO)_4]$ | 59 1 | 1 0 | 165 |
| $[(C_2H_5)_4N]_2[Co(NCO)_4]$ | 55 0 | 1 0 | 165 |
| $[(C_2H_5)_4N]_2[Ni(NCO)_4]$ | 55.8 | 1.0 | 165 |
| $[(C_2H_5)_4N]_2[Cu(NCO)_4]$ | 53 1 | 1 0 | 165 |
| $[(C_2H_5)_4N]_2[Zn(NCO)_4]$ | 54 0 | 1 0 | 165 |
| $[(C_6H_5)_4As]_2[Ni(NCO)_4]$ | 83 0 ? | 0 884 | 35 |
| $[(n\text{-}C_4H_9)_4N]_2[Zn(NCSe)_4]$ | 58 2 | 1.0 | 166 |
| $[(n\text{-}C_4H_9)_4N]_2[VO(NCSe)_4]$ | 47 0 | 1 0 | 167 |
| $[(n\text{-}C_4H_9)_4N]_2[Pd(NCSe)_4]$ | 52 0 | 1 0 | 168 |
| $[(n\text{-}C_4H_9)_4N]_2[Pt(NCSe)_4]$ | 52 0 | 1 0 | 168 |
| $[(n\text{-}C_4H_9)_4N]_2[Cd_2(NCSe)_6]$ | 42 0 | 1 0 | 168 |
| $[(C_2H_5)_4N]_2[FeCl_4]$ | 47 0 | 1 0 | 169 |
| $[(C_6H_5)_3CH_3As]_2[NiCl_4]$ | 56 0 | 0 5 | 21 |

TABLE 5 (contmued)

| Complex | $\Lambda_M$ | $c \times 10^3$ | Ref. |
|---|---|---|---|
| $[(C_6H_5)_3CH_3As]_2[NiI_4]$ | 53 0 | 0 5 | 21 |
| $[(C_6H_5)_3CH_3As]_2[CoCl_4]$ | 55 0 | 0 5 | 21 |
| $[(C_6H_5)_3CH_3As]_2[CoBr_4]$ | 54 0 | 0 5 | 21 |
| $[(C_6H_5)_3CH_3As]_2[CoI_4]$ | 53 0 | 0 5 | 21 |
| $[(C_6H_5)_3CH_3As]_2[MnCl_4]$ | 57 0 | 0 5 | 21 |
| $[(C_6H_5)_3CH_3As]_2[ZnCl_4]$ | 53.0 | 0 5 | 21 |
| $[(C_6H_5)_3CH_3As]_2[CuCl_4]$ | 60 0 | 0 5 | 21 |
| $[(C_6H_5)_4P]_2[NiBr_4]$ | 61 7 | 1.0 | 43 |

[a] Values extrapolated at $10^{-3}$ *M.*

Complexes of the first type are notable since they include one of the earliest determinations of $\Lambda_M$ in nitrobenzene; this is the investigation by Nyholm [184] of the diphenylmethylarsine oxide complexes of copper(II) Other important papers [185,186] are concerned with lanthanide complexes $[LnL_7](ClO_4)_3$, and $[LnL_8](ClO_4)_3$, (L = dimethyl sulphoxide, pyridine-*N*-oxide), and these are considered in more detail in the section on

TABLE 6

Molar conductivity in nitrobenzene of 3 1 and 4 1 electrolytes containing an uncomplexed cation and a complex anion of pseudohalide ligands [a]. Concentration· $10^{-3}$ *M.*

| Complex | $\Lambda_M$ | Ref |
|---|---|---|
| $[(n\text{-}C_4H_9)_4N]_3[V(NCSe)_6]$ | 66 0 | 167 |
| $[(n\text{-}C_4H_9)_4N]_3[Pr(NCS)_6]$ | 82 4 | 166 |
| $[(n\text{-}C_4H_9)_4N]_3[Nd(NCS)_6]$ | 77.8 | 166 |
| $[(n\text{-}C_4H_9)_4N]_3[Sm(NCS)_6]$ | 76.6 | 166 |
| $[(n\text{-}C_4H_9)_4N]_3[Dy(NCS)_6]$ | 72 7 | 166 |
| $[(n\text{-}C_4H_9)_4N]_3[Ho(NCS)_6]$ | 66 7 | 166 |
| $[(n\text{-}C_4H_9)_4N]_3[Er(NCS)_6]$ | 72 1 | 166 |
| $[(n\text{-}C_4H_9)_4N]_3[Fe(NCS)_6]$ | 83 7 | 166 |
| $[(n\text{-}C_4H_9)_4N]_3[Fe(NCSe)_6]$ | 66 0 | 168 |
| $[(n\text{-}C_4H_9)_4N]_3[Y(NCSe)_6]$ | 68.0 | 168 |
| $[(n\text{-}C_4H_9)_4N]_3[Rh(NCSe)_6]$ | 70.0 | 168 |
| $[(n\text{-}C_4H_9)_4N]_4[Mn(NCSe)_6]$ | 90.0 | 168 |
| $[(n\text{-}C_4H_9)_4N]_4[Ni(NCSe)_6]$ | 98 0 | 168 |

[a] None of the corresponding halo-complexes appears to have been studied.

TABLE 7

**Molar conductivity in nitrobenzene of electrolytes having an uncomplexed cation and a complex anion containing unidentate ligands only. Concentration: $10^{-3}$ *M*.**

| *Complex* | $\Lambda_M$ | *Ref.* |
|---|---|---|
| $[(t\text{-}C_4H_9)_4N][NiBr_3(C_6H_5)_3P]$ | 23 3 | 43 |
| $[(C_2H_5)_4N][PtBr_3(NH_3)]$ | 24 0 | 170 |
| $[(C_2H_5)_4N][PtI_3(NH_3)]$ | 26.0 | 170 |
| $[(C_2H_5)_4N][PtBr_3(\text{pyridine})]$ | 25.0 | 170 |
| $[(C_2H_5)_4N][PtI_3(\text{pyridine})]$ | 25.0 | 170 |
| $[(C_2H_5)_4N][PtI_3(2\text{-picoline})]$ | 27 0 | 170 |
| $[(C_2H_5)_4N][PtBr_3(\text{piperidine})]$ | 24.0 | 170 |
| $[(C_2H_5)_4N][PtI_3(\text{piperidine})]$ | 24 0 | 170 |
| $[(C_2H_5)_4N][PtBr_3(C_2H_5NH_2)]$ | 24 0 | 170 |
| $[(C_2H_5)_4N][PtI_3(C_2H_5NH_2)]$ | 27.0 | 170 |
| $[(C_2H_5)_4N][PtBr_3(C_2H_5)_2S]$ | 25.0 | 170 |
| $[(C_2H_5)_4N][PtI_3(C_2H_5)_2S]$ | 24 0 | 170 |
| $[(C_2H_5)_4N][PdBr_3(C_2H_5)_2S]$ | 24.0 | 170 |
| $[(C_2H_5)_4N][FeCl_3(\text{quinoline})]$ | 26.0 | 169 |
| $[(C_2H_5)_4N][FeBr_3(\text{quinoline})]$ | 27 0 | 169 |
| $[(C_2H_5)_4N][FeCl_3(3\text{-methylisoquinoline})]$ | 28 5 | 169 |
| $[(C_2H_5)_4N][FeBr_3(3\text{-methylisoquinoline})]$ | 28 0 | 169 |
| $[(n\text{-}C_4H_9)_4N][Rh(CO)_2Cl_2]$ | 29 5 | 171 |
| $[(n\text{-}C_4H_9)_4N][Rh(CO)_2Br_2]$ | 29.1 | 171 |
| $[(C_6H_5)_4As][Rh(CO)_2Cl_2]$ | 29.2 | 171 |
| $[(C_6H_5)_4As][Rh(CO)_2Br_2]$ | 28 3 | 171 |
| $[(C_6H_5)_4As][Rh(CO)_2I_2]$ | 25 5 | 171 |
| $[(n\text{-}C_4H_9)_4N][W(CO)_3I_3\{(C_6H_5)_3P\}]$ | 20.0 | 42 |
| $[(n\text{-}C_4H_9)_4N]_2[Rh_2(CO)_2Br_4]$ | 33.8 | 42 |
| $[(C_6H_5)_4As]_2[Rh_2(CO)_2Br_4]$ | 36 5 | 42 |
| $[(CH_3)_4N]_2[RuCl_2(CO)_2(SnCl_3)_2]$ | 55 0 | 172 |
| $[(C_6H_5)_4As]_2[RuBr_2(CO)_2(SnBr_3)_2]$ | 56.0 | 172 |

lanthanide complexes. An interesting example [187] concerns the $Mo_6Cl_8$ cluster compounds with triphenylphosphine oxide and triphenylarsine oxide. On the basis of the $\Lambda_M$ values (and other data) these are formulated with the oxide in the cation; thus the compound $H_2[(Mo_6Cl_8)Cl_6].4(C_6H_5)_3PO$ is proposed as $[\{(C_6H_5)_3PO\}_2H]_2[(Mo_6Cl_8)Cl_6]$. For other papers on oxide donors see refs. 188–190.

TABLE 8

Molar conductivity in nitrobenzene of selected non-complex compounds used for reference purposes Concentration $10^{-3}$ *M* except where otherwise specified.

| *Compound* | $\Lambda_M$ | *Ref* |
|---|---|---|
| $[(C_{12}H_{11})_2(CH_3)_2N]Cl$ | 18 8 [a] | 173 |
| $[(C_{12}H_{11})_2(CH_3)_2N]Cl$ | 20.1 [b] | 173 |
| $[(n\text{-}C_4H_9)_4N]Br$ | 24 8 | 166 |
| $[(n\text{-}C_4H_9)_4N]NCS$ | 38.8 | 166 |
| $[(n\text{-}C_4H_9)_4N]Br$ | 27 0 | 164, 174 |
| $[(n\text{-}C_4H_9)_4N]I$ | 30 0 | 164, 174 |
| $[(n\text{-}C_4H_9)_4N]NO_3$ | 31 4 [c] | 159 |
| $[(n\text{-}C_4H_9)_4N]Br$ | 30 0 [c] | 159 |
| $[(n\text{-}C_4H_9)_4N](CH_3COO)$ | 31.0 [c] | 159 |
| $[(C_2H_5)_4N]Cl$ | 34.0 [c] | 159 |
| $[(n\text{-}C_4H_9)_4N][BF(C_6H_5)_3]$ | 21 4 [c] | 175 |
| $[(n\text{-}C_4H_9)_4N]ClO_4$ | 31 0 | 176 |
| $[(n\text{-}C_4H_9)_4N]NO_3$ | 30 5 | 176 |
| $[(C_2H_5)_4N]ClO_4$ | 33 0 | 22 |
| $[(C_2H_5)_4N]ClO_4$ | 35 0 | 177 |

[a] $10^{-4}$ *M* [b] $4 \times 10^{-5}$ *M* [c] Values interpolated at $10^{-3}$ *M*.

Because of the tendency of β-diketones to give neutral complexes, there have been few examples of useful $\Lambda_M$ measurements, although one interesting example [191] is the series $[(\pi\text{-}Cp)_2TiL]ClO_4$ for which the values are slightly high for 1 1 electrolytes. A typical example of the problems inherent in the use of conductivity data is the lack of agreement in published values for $[Ti(acac)_3][FeCl_4]$ In the course of an investigation of β-diketone complexes of the general formula $[ML_3][M'Cl_4]$ and $[ML_3][M''Cl_6]$ (M' = Fe, Au, M'' = Sb) values of $\Lambda_M$ = 24 8 and 27 0 $ohm^{-1}$ $cm^2$. $mole^{-1}$ were found [112] for $[Ti(acac)_3][FeCl_4]$ at $10^{-3}$ *M* Almost concurrently a report of $\Lambda_M - c^{1/2}$ data for the same complex in various solvents was published [111]; this shows values ranging from $\Lambda_M$ = 37 5 $ohm^{-1}$. $cm^2$. $mole^{-1}$ at $0.54 \times 10^{-3}$ *M* to 30.8 $ohm^{-1}$. $cm^2$. $mole^{-1}$ at $8\ 65 \times 10^{-3}$ *M*. The report suggests that the values are lowered by small amounts of water. Differences in the order of 50% for systems of this type are disturbing

Complexes of the ligands containing both oxygen and other donor atoms have been studied [192,193].

*(iii) Nitrogen donors*

Complexes of nitrogen donors for which $\Lambda_M$ data are available comprise the largest single group of compounds in this review. The data for simple unidentate donors such as the pseudohalide ions, amines, and heterocyclic compounds are in Tables 5–7 as reference values and have been discussed as such in section E(i)

Most of the data for bidentate ligands are concerned with complexes of bipyridyl and *o*-phenanthroline and related ligands. It is particularly noteworthy that the earliest significant paper [183] for a complex in nitrobenzene was on the system $[Au(bipy)(C_2H_5)_2][(C_2H_5)_2AuBr_2]$. Other early $\Lambda_M$ values used for reference purposes are given by Harris [194] and by Martin and Waind [180]. The latter paper has been discussed in the introduction. Typical examples of the use of conductivity measurements for complexes of bipyridyl and *o*-phenanthroline with both transition and non-transition elements, covering all charge types, are in refs. 30, 62, 63, 65, 66, 158, 195, and 196. A more recent example of interest is the investigation [?76] of complexes of P, As, and Sb, thus $PCl_5$ phen, and $AsCl_5.SbCl_5$ phen are formulated as $[PCl_4(phen)]Cl$ and $[AsCl_4(phen)][SbCl_6]$, respectively Geometrical isomers of the type *cis*- and *trans*-$[Ir(phen)_2X_2]X$ have been studied [64], the *cis* isomer being a 1 1 electrolyte and the *trans* isomer being insoluble.

For substituted bipyridyl and phenanthroline systems the most valuable source of information is the series of papers by Hall and co-workers [22,68,69,177,197] which are concerned with complexes of 2,9-dimethyl-1,10-phenanthroline, and 4,6,4′,6′-tetramethyl-2,2′-bipyridyl.

The other source of detailed $\Lambda_M$ data for bidentate nitrogen donors is the work of Sutton on complexes of 2-aminomethylpyridine and the 6-methyl derivative (see, for example, ref. 150 and references therein).

For tridentate systems the most commonly investigated ligand has been terpyridyl [71,198] For more complex systems the papers of most interest in the light of current developments are those of Ciampolini et al. [174], Geldard and Lions [199], and Chiswell and Lions [200]. The first is concerned with complexes [Co(trenMe)X] X (trenMe = tris-(2-dimethylaminoethyl)amine, X = halide, $NO_3^-$, $ClO_4^-$) for which the $\Lambda_M$ data are used to support a five-coordinate structure. The latter two papers describe measurements for complexes of the ligands PAPHY (pyridine-2-aldehyde-2′-pyridylhydrazone) and butane-2,3-dionebis (2′-pyridylhydrazone) respectively, now recognised as so-called "suspect" ligands A further paper in the same series [201] describes the cobalt complexes of ligands related to PAPHY, and a more recent paper [202] on complexes of PAPHY discusses some anomalously low $\Lambda_M$ values. For other complexes of heterocyclic ligands see refs 203–207

*(iv) Phosphorus donors*

Despite the intense interest in the complexes of phosphorus donor ligands, there are surprisingly few conductivity data for complexes containing only unidentate phosphorus ligands Triphenylphosphine as a ligand in some gold complexes [208] and some nickel complexes [43] have been studied, as have some chloro-bridged ruthenium complexes containing substituted phosphines [209] Mann and co-workers [210] have recorded $\Lambda_M$ values for some twenty complexes of the general formula $[ML_3X]X'$, where M = Pt, Pd; X = $Cl^-$, $Br^-$, $I^-$, $SCN^-$, $ClO_4^-$; X′ = X, picrate, and L = diethylphenylphosphine, 2-phenylisophosphindole. Tertiary phosphines have been widely used in substituted carbonyl, nitrosyl, and hydride complexes. The other unidentate phosphorus donor which has been studied is the cyclic phosphite ester $P(OCH_2)_3CCH_3$, $\Lambda_M$ values for the copper(I) and silver(I) complexes [211] and for the cobalt(I) complexes [176] having been reported

Far more data are available for complexes of polydentate phosphorus donors, the most valuable series of measurements is for the complexes [MLX] X′, where M = Pt, Pd, Ni, Fe, X = X′ = $Cl^-$, $Br^-$, $I^-$, $ClO_4^-$, $SCN^-$, $CN^-$, $(C_6H_5)_4B^-$, L = tris-(*o*-diphenylphosphinophenyl)phosphine [212–215]. As in the case of the corresponding arsenic donors, these complexes show clearly the various anion effects Some values for other polydentate ligands are in refs 94, and 216–218, and for the widely investigated ligand 1,2-bisdiphenylphosphinoethane (diphos) in refs 115, 217, and 219. Thus, Carty [115] has discussed the complexes $GaX_3$ . ½ diphos, and has used conductivity data to support the dimeric formula $[Ga(diphos)_2X_2]$ $[GaX_4]$

Complexes in which phosphorus acts as a donor atom in conjunction with other donors such as nitrogen [220], sulphur [221], and arsenic [222] have been studied

### *(v) Arsenic donors*

As would be expected from the great interest in the structures of complexes formed by ligands having arsenic donor atoms, much information on the conductivity of such complexes has been accumulated Much of the earlier work was carried out by Nyholm and co-workers on diarsine complexes e g see refs 21, 223–226), and the data obtained have frequently been quoted as typical of given electrolyte types. Particularly widely used in this respect have been the values given by Gill and Nyholm [21], and Harris and Nyholm [224]. Except where there are uncertainties introduced by both cation and anion being complex [225], the values of $\Lambda_M$ are within the ranges suggested in this review Carbonyl complexes partially substituted by diarsine are considered separately.

More recently, there has been considerable interest in complexes containing tri- and tetradentate arsenic ligands, particularly because the steric requirements of the ligands impose restrictions on the structure of the complexes, and thus in some cases on the electrolyte type. Particularly noteworthy are the complexes [MLX] X′, where M = Pt, Pd, Ni, X = X′ = $Cl^-$, $Br^-$, $I^-$, $SCN^-$, $CN^-$, $ClO_4^-$, $(C_6H_5)_4B^-$, L = tris(*o*-diphenylarsinophenyl) arsine. The data given [213,227,228] for complexes of this type form the basis for the typical values for 1.1 electrolytes, and also for the observation of anionic effects Thus, [PtLCl] $ClO_4$ and [PtLCl] $\{(C_6H_5)_4B\}$ have $\Lambda_M$ = 27.0 and 17 4 $ohm^{-1}$ . $cm^2$ . $mole^{-1}$ respectively at $c = 10^{-3}$ *M* [227]. Complexes of this type have also been investigated by Nyholm [124].

There is much information available for complexes containing arsenic donor atom(s) together with other donors such as nitrogen, sulphur, and phosphorus Typical examples are in refs 129, 163, 193, 222, 229, and 230 An interesting example is the recent paper of Chiswell and Lee [193] who use $\Lambda_M$ data for complexes $Co_3L_4X_4(H_2O)_2$ (L = *N*-*o*-dimethylarsinophenylsalicylaldimine, X = $Cl^-$, $Br^-$, $SCN^-$) to support a formulation $[CoL_2]_2[CoX_4]2H_2O$ containing both $Co^{II}$ and $Co^{III}$.

*(vi) Carbonyls and nitrosyls*

Conductivity data for substituted carbonyl and nitrosyl complexes, for both complex cationic and complex anionic species, are readily available. Reference may particularly be made to the work of Lewis, Nyholm and co-workers[231–236] For example, refs 231–233 contain data for some fifteen complexes of Cr–Mo–W with different combinations of CO, diarsine, and halide, e g. $[Mo(diars)_2(CO)_2X]X$ The $\Lambda_M$ values fall exactly into the range for 1 1 electrolytes, the values given[235] for the systems $[M(CO)_3LX]X$ (M = Mo, W; L = triarsine, X = $I^-$, $(C_6H_5)_4B^-$) are interesting in being one of the few examples of measurements in $10^{-1}$ *M* solution. They are also used as proof of a seven-coordinate system. The values reported by Venanzi and co-workers[237,238] provide further evidence for the lowering of $\Lambda_M$ caused by the low ionic mobility of the tetraphenylborate anion. Additional data for a variety of cationic carbonyl complexes are in refs. 239–242.

A particularly useful example for anionic carbonyl complexes with a quaternary ammonium cation is the paper of Hawkes and Ginsberg[179] Detailed data and plots of $\Lambda$ versus $c^{1/2}$ are given for the complexes of the type $[(C_2H_5)_4N]_2[Re(CO)_3X_3]$, and the slopes of the linear plots are satisfactorily correlated with theoretical values The values for complexes of the type $[(C_2H_5)_4N]_2[Re_2(CO)_6X_4]$ indicate decomposition or ion-pairing. Data for somewhat related systems are given in refs. 171 and 172.

Nitrosyl complexes which appear to fall into the accepted range of $\Lambda_M$ values include systems such as $[Co(NO)_2L_2]X$, (L = triphenylphosphine, ½ diphos, X = $Cl^-$, $ClO_4^-$, $(C_6H_5)_4B^-$)[243] and $[Fe(NO)(CO)_2L_2]X$ (L = triphenylphosphine, X = $PF_6^-$, $BF_4^-$, $NO_3^-$, $Cl^-$, $Br^-$, $I^-$)[244].

*(vii) Sulphur donors*

One of the earliest examples of the determination of $\Lambda_M$ for a complex in nitrobenzene was the investigation of $[NiL_3](ClO_4)_2$, where L = 1,2-dimethylthioethane)[245] for which a value of 41 5 $ohm^{-1}.cm^2.mole^{-1}$ was found at $c = 3.57 \times 10^{-5}$ *M*. This value is rather low in relation to data for most other systems. There have been surprisingly few determinations on complexes containing ligands with sulphur as the only donor atom. One interesting example is the investigation of isomers of $[IrL_3Cl_3]$ (L = diethylsulphide)[246] conductimetrically and in conjunction with other methods The substituted carbonyl complexes $[RuL_3(CO)_2(SnCl_3)]X$ (L = diethylsulphide; X = $Cl^-$, $(C_6H_5)_4B^-$)[241] have been measured ($\Lambda_M$ = 19 and 15 $ohm^{-1}.cm^2.mole^{-1}$, respectively).

The majority of other complexes which have been investigated are those formed by chelating ligands in which the sulphur is a donor atom in conjunction with one or more of nitrogen, arsenic, and phosphorus. Typical examples include the complexes of 2-thioamidopyridine investigated by Sutton[150,151,247,248], the values of $\Lambda_M$ are generally in agreement with the ranges suggested earlier Much information on this type of system has been published by Livingstone and co-workers and typical data are in refs. 85, 148, 230, 249, and 250. Other mixed nitrogen–sulphur ligands which have been studied include di-(2-pyridyl)sulphide[152] and 1-allyl-3-(2-pyridyl)-2-thiourea[251]. Finally, reference should be made to the excellent investigation [178] of bis(*N,N*-di-n-butyldithiocarbamato) gold(III) dibromoaurate(I), for which detailed $\Lambda_M - c^{1/2}$ data are given and carefully interpreted.

*(viii) Lanthanide complexes*

As in section D(viii), these complexes provide a useful source of data for 3:1 electrolytes. There have been at least three recent investigations of the conductivity of such complexes [185,186,192]; the complexes $[LnL_8](ClO_4)_3$ (L = pyridine-*N*-oxide) [186] have $\Lambda_M$ values in the range 79.2–83.6 $ohm^{-1}.cm^2.mole^{-1}$, with an average value of 81.3 $ohm^{-1}.cm^2.mole^{-1}$. The dimethylsulphoxide complexes $[LnL_8](ClO_4)_3$ and $[LnL_7](ClO_4)_3$ have very similar $\Lambda_M$ values, and although the authors [185] use molecular weight data to support their suggestion that the DMSO is unlikely to be coordinated in nitrobenzene this does not appear to invalidate the $\Lambda_M$ data. A rather more complex series of compounds of the ligand ethylenediamine-bis-acetylacetone, e.g. $[LnL_2]X_3$, have values [192] in the range 72–81 $ohm^{-1}.cm^2.mole^{-1}$, with an average of 80 $ohm^{-1}.cm^2.mole^{-1}$ at $10^{-3}$ *M*. See also the values in ref. 166 of Table 6.

*(ix) Miscellaneous complexes*

There have been several investigations of cluster compounds, thus, complexes containing the $Mo_6Cl_8$ unit have been investigated by Sheldon [187,252] and by Fergusson et al. [377]. The values obtained (average $\Lambda_M \sim 51$ $ohm^{-1}.cm^2.mole^{-1}$ at $10^{-3}$ *M*) are only slightly less than expected for 2:1 electrolytes. Bridged complexes have also been investigated, and a notable example is the series of complexes containing the $[L_3RuCl_3RuL_3]^+$ cation studied by Chatt and Hayter [209]. In this case the value of $\Lambda_M$ is again slightly low, however, the values for another bridged cation, $[L_4Cu_2BH_4]^+$, are correspondingly higher [253]. Values for other non-bridging hydride complexes have been reported [219,254]. Complexes containing metal cyclopentadienyl systems have been investigated, notably by Doyle and Tobias [191,255,256], the values of $\Lambda_M$ being well in line with the ranges suggested in this review. Mixed metal complexes of the general type $[M^I(M^{II}L)_2](ClO_4)_2$ were shown [257] to have $\Lambda_M$ values lower than for 2:1 electrolytes. A very unusual compound which was the subject of a recent investigation is $Ti\{N(CH_3)_2\}_4 \cdot 2B_{10}H_{14}$, this has $\Lambda_M \sim 10$ $ohm^{-1}.cm^2.mole^{-1}$ in dilute solution, which is claimed to be "suggestive of an ionic structure" [258]. Possible structures suggested were $[Ti\{N(CH_3)_2\}_2]$-$[B_{10}H_{13}(CH_3)_2NH]_2$ and $[Ti\{N(CH_3)_2\}_2\{(CH_3)_2NH\}_2][B_{10}H_{13}]_2$. However, these are both 2:1 electrolytes, and the low value of $\Lambda_M$ indicates that they could only be present to a small extent.

## F. ACETONE

*(i) General considerations and non-complex electrolytes*

The position in relation to the conductivity of complexes in this solvent is perhaps more confusing than for any other organic solvent. Published data vary widely, even over comparable concentration ranges As an example, for the apparently simple electrolyte $(C_6H_5)_4As.NCO, 2H_2O$, a value of $\Lambda_M$ = 229 $ohm^{-1}.cm^2.mole^{-1}$ is quoted [40] which is far higher than the values quoted [259] ($\Lambda_M$ = 146–167 $ohm^{-1}.cm^2.mole^{-1}$) for a series of complexes $[ML_3](ClO_4)_2$ (M = Mn–Zn, L = diacetamide) at comparable concentrations, although the latter are 2.1 electrolytes

The most widely used reference values are those of Reynolds and Kraus [260] who give detailed data for a series of 1·1 electrolytes over wide concentration ranges The compounds studied were alkylammonium and alkali metal salts, values interpolated from the data given for $10^{-3}$ *M* range from ca. 100–160 $ohm^{-1}$ $cm^2.mole^{-1}$, with an average value (13 compounds) of 137 $ohm^{-1}.cm^2.mole^{-1}$ A value of 123 $ohm^{-1}.cm^2.mole^{-1}$ ($10^{-3}$ *M*) is quoted [261] for $(n\text{-}C_4H_9)_4NBr$, and 154 $ohm^{-1}$ $cm^2$ $mole^{-1}$ for $(C_6H_5)_4AsCl$ at 0.5 × $10^{-3}$ *M* [262]. No satisfactory reference values for 2:1 or 3.1 electrolytes are available.

*(ii) Uniunivalent electrolytes*

Reference to Table 9 shows the wide range of values obtained. It is most convenient to consider the various concentration ranges separately At $10^{-3}$ *M*, an average value for the data is 120 $ohm^{-1}.cm^2$ $mole^{-1}$, though attention is again drawn to the lower values arising [264] for compounds containing the tetraphenylborate anion. It is interesting that this average value is exactly that quoted earlier [283] for complexes which are 1 1 electrolytes in this solvent. At lower concentrations (~ $10^{-4}$ *M*) an average value of 135 $ohm^{-1}$ $cm^2.mole^{-1}$ appears reasonable The most detailed investigation over a concentration range is that of Deacon and West [270].

*(iii) Bisunivalent electrolytes*

The position for these electrolytes is less clear than for 1 1 electrolytes (Table 10) For $10^{-3}$ *M* solutions the most reliable data are probably those in refs 92 and 280, and hence an average $\Lambda_M$ value of ~ 180 $ohm^{-1}.cm^2.mole^{-1}$ results The low values for the acetamide complexes mentioned in section F(i) [259] are probably due to ion association At $10^{-4}$ *M* the values given in the most comprehensive investigation [276] (average $\Lambda_M$ = 242 $ohm^{-1}$ $cm^2.mole^{-1}$) do not agree well with the remaining values [277] (average $\Lambda_M$ = 320 $ohm^{-1}.cm^2.mole^{-1}$), and because of this, an average value at this concentration of 272 $ohm^{-1}$ $cm^2.mole^{-1}$ may not be well-founded However, very recently a further series of dithiolene complexes (6 values, average $\Lambda_M$ = 266 $ohm^{-1}.cm^2.mole^{-1}$) does support this average value [284]

*(iv) Trisunivalent electrolytes*

The only compound for which a value of conductivity is given [137] is $[(C_6H_5)_4P]_3$ $[Co(maleonitriledithiolate)_3]$ for which $\Lambda_M$ = 446 $ohm^{-1}.cm^2$ $mole^{-1}$ at $10^{-4}$ *M* Comparisons with data for other electrolyte types at this concentration suggest that this is a reasonable value

TABLE 9

Molar conductivity in acetone of selected 1.1 electrolytes (complex compounds)

| System | Range $\Lambda_M$ | No of values | $c \times 10^3$ | Comments | Ref |
|---|---|---|---|---|---|
| $[M(CO)_2(diphos)_2I]I$ | 144, 156 | 2 | 0 5 | M = Mo, W | 263 |
| $[M(CO)_3LCl](C_6H_5)_4B$<br>$[M(CO)_2L_2Cl](C_6H_5)_4B$ | 89 7 -107 2 | 9 [a] | 1 0 | M = Mo, W; L = bi- or tridentate As, N ligands | 264 |
| $[C_5H_5CoLL']X$ | 118 -136 | 8 [b] | 1 0 | L = bidentate P ligand, L′ = fluoroalkyl, X = I, $PF_6$ | 265 |
| $[C_5H_5Mo(CO)_2L_2]X$<br>$[C_5H_5Mo(CO)_2L']X$ | 109 -193 | 4 | 0 7 -1 8 | L = phosphine, L′ = bidentate P, As ligand | 266 |
| $[Ru_2Cl_3L_6][RuCl_3L_6]$ | 108 | 1 | 0 64 | L = diethylphenylphosphine | 267 |
| $Na[M(CO)_5(SO_2C_6H_5)]$ | 80, 95 | 2 | 1 0 | M = Cr, W | 268 |
| $[CoL_5ClO_4]$ | 118 | 1 | 1 0 | L = complex phosphite ester | 261 |
| $(C_2H_5)_4N[Mo(CO)_3\{R(C_6H_5)_3\}X_3]$ | 107 -185 | 6 | 0 88 -1 18 | R = P, As, Sb; X = Cl, Br | 269 |
| $(CH_3)_4R[HgI_3]$ | 165, 166 | 2 | 0 9 | R = P, N | 270 |
| $(C_2H_5)_4N[M(CO)_4X_3]$ | 110 -157 | 4 | 094 -1 18 | M = Mo, W, X = Cl, Br | 271 |
| $(C_2H_5)_4N[NiLBr_3]$ | 125 | 1 | 1 0 | L = benzimidazole | 41 |
| $R_4M[CdCl_3L]$ | 101 -125 | 3 | ? | R = $C_2H_5$, $C_6H_5$, M = N, As, P, L = thiourea | 272 |
| $[ReH_4L_2]X$<br>$[ReH_4LL'_2]X$ | 93 -129 | 8 | ? | L = diphos, L′ = $(C_6H_5)_3P$ | 273 |
| $[C_5H_5Mo(CO)_2L_2][C_5H_5Mo(CO)_3]$<br>$[C_5H_5Mo(CO)_2L'][C_5H_5Mo(CO)_3]$ | 85 -108 | 4 [c] | 1 0 | L = tert -phosphines, L′ = diphos | 274 |
| $[Mo(CO)_2L_2I]X$ | 154 -175 | 3 | 0 5 -0 8 | L = *o*-phen , bipy, X = I, $I_3$ | 275 |
| $R[ML_2Y]$ | 103 -168 | 31 [d] | 0 1 | R = $(C_6H_5)_4P$, $(C_2H_5)_4N$, $(C_4H_9)_4N$, M = Fe, Co, Y = miscellaneous ligands, L = dithiolenes | 277 |
| $R[C_5H_5Mn(NO)L]$ | 123 -172 | 6 [e] | 0 1 | R = $(C_6H_5)_4P$, $(C_2H_5)_4N$, L = dithiolenes | 278 |
| $[(C_6H_5)_4P][C_5H_5MoL_2]$ | 126 | 1 | 0 1 | L = maleonitriledithiolene | 137 |
| $[Ir(CO)(CS_2)L_3](C_6H_5)_4B$ | 200 | 1 | 0 01 | L = $(C_6H_5)_3P$ | 279 |

Average values [a] 95.4, [b] 127 0, [c] 92 5; [d] 133 1, [e] 145 8 $ohm^{-1}$ $cm^2$ $mole^{-1}$

TABLE 10

Molar conductivities in acetone of 2 1 electrolytes (complex compounds). Concentration $10^{-3}M$.

| System | Range $\Lambda_M$ | No of values | Comments | Ref |
|---|---|---|---|---|
| $[NiL_6](ClO_4)_2$ | 238–298 | 3 | L = complex phosphite esters | 261 |
| $[ML_6](ClO_4)_2$ | 183, 201 | 2 | L = lactam, M = Co, Ni | 92 |
| $R_2[ML_2]$ | 157–188 | 3 | R = $(C_2H_5)_4N$, $(C_4H_9)_4N$, L = dithiolene | 280 |
| $[ML_3](ClO_4)_2$ | 146–167 | 6[a] | M = Mn–Zn, L = diacetamide | 259 |
| $R_2[ML_3]$ | 206–288 | 8[b, c] | M = Ti, V, Cr, W, Mn, Re, Fe, L = dithiolene, R = $(C_6H_5)_4As$, $(C_2H_5)_4N$, $(C_4H_9)_4N$ | 276 |
| $[(n\text{-}C_4H_9)_4N]_2[FeL_2X]$ | 287–344 | 3[c] | L = dithiolene, X = NCO, $N_3$, CN | 277 |
| $[NiL](PF_6)_2$ | 323 | 1[c] | L = quadridentate N ligand | 281 |
| $[(C_6H_5)_4As]_2[Re_2L_4]$ | 309 | 1[d] | L = dithiolene | 282 |

[a] Average value 155 0 $ohm^{-1}$ $cm^2$ $mole^{-1}$ [b] Average value 242 0 $ohm^{-1}$ $cm^2$ $mole^{-1}$
[c] $10^{-4}$ *M*. [d] 0 22 X $10^{-3}$ *M*

### *(v) Other data*

An interesting investigation is that of Cousins and Hart [285], who plot equivalent conductivity against ionic radius for the lanthanide ions in the complexes $ML_4(NO_3)_3$, where L is triphenylarsine oxide. The values increase steadily from 45 $ohm^{-1}$ $cm^2$. $mole^{-1}$ for La to 130 $ohm^{-1}$ $cm^2$ $mole^{-1}$ for Yb This is considered to be due to steric effects on the equilibrium

$$[ML_4(NO_3)_3] \rightleftharpoons [ML_4(NO_3)_2]^+ + NO_3^-$$

There are several other sets of data which have not been considered in arriving at average values, these have normally been excluded when the data are so far outside the common ranges as to indicate some unusual effect. Examples are the $\Lambda_M$ values given for $[C_5H_5CrC_7H_7]PF_6$ (256 $ohm^{-1}$. $cm^2$. $mole^{-1}$ at 1 13 X $10^{-4}$ *M*) [286], and for $[C_5H_5Re(CO)_3Cl][SbCl_6]$ (242 ± 5 $ohm^{-1}$ $cm^2$. $mole^{-1}$ at 1.4 – 3 0 X $10^{-4}$ *M*) [287]. Behrens and Rosenfelder [275] consider the high values for compounds $[Mo(CO)_2L_2I]I$ to be due to dissociation of the type

$$[Mo(CO)_2L_2I]^+ \rightleftharpoons [Mo(CO)_2L_2]^{2+} + I^-$$

For further data in acetone see refs. 288–291.

## G ACETONITRILE

*(i) General considerations*

This solvent has been extensively used in conductivity studies, notably because of its low viscosity and high dielectric constant relative to other solvents [292]. However, the coordinating power of $CH_3CN$, and the dissociative and solvolytic effects with frequently occur, are major disadvantages and have recently led many workers to prefer nitromethane.

The coordinating properties of acetonitrile have been reviewed [293], and there is ample evidence for the formation both of solid complexes and of complexes in solution. A representative example [294] since Walton's review is the isolation of $TiCl_2(CH_3CN)_2$ and $TiBr_2(CH_3CN)_2$, these complexes are non-conducting in $CH_3CN$.

Recognition of the difficulties of using acetonitrile has led to a proportionately greater number of definitive and detailed studies, particularly of concentration effects, than for other solvents One of the earliest [295] concerned some $Cu^{II}$ salts and complexes with $CH_3CN$ itself. More recent examples include some dithiolene complexes [296], heterocyclic *N*-oxide complexes $[ML_6](ClO_4)_2$ [109], and zinc tris(2-aminoethyl)amine halides [11]. Cotton and co-workers [292] have investigated a number of anionic rhenium complexes, as have Hawkes and Ginsberg [179], and Walton [297] has reported a praticularly detailed study of some tetrahalo- and neutral $Tl^{III}$ complexes. However, the best discussion is probably that of Beattie et al. [298] who point out differences in results and errors in interpretation due to both solvent and solute problems, and review the experimental procedure which may be necessary for some systems. This paper also describes a rigorous method of purification for acetonitrile

*(ii) Acceptable $\Lambda_M$ ranges for various electrolyte types*

For non-complex compounds of the 1:1 electrolyte type, mainly tetraalkylammonium salts, the most widely used data are those of Harkness and Daggett [299] and of Coetzee and Cunningham [14] Combination of these data with those of other workers [261,300–303] leads to an average $\Lambda_M$ value of ~ 159 $ohm^{-1}$ $cm^2$. $mole^{-1}$ at ~ $10^{-3}$ *M*, though, as usual, values for tetraphenylborate salts are significantly lower [14]. When the compilation is extended to complexes the problem is immediately apparent, values as low as 92 and as high as 199 $ohm^{-1}$. $cm^2$. $mole^{-1}$ having been used to characterise 1 1 electrolytes. A form of successive approximation procedure leads to an average value of ~ 140 $ohm^{-1}$. $cm^2$. $mole^{-1}$ at ~ $10^{-3}$ *M*, and for complexes the range suggested by Walton [293] (120–160 $ohm^{-1}$. $cm^2$. $mole^{-1}$) is acceptable

The situation for 2:1 electrolytes is even more difficult, values as low as 145 and as high as 336 $ohm^{-1}$. $cm^2$ $mole^{-1}$ having been used. Successive approximation leads to an average value of ~ 263 $ohm^{-1}$. $cm^2$ $mole^{-1}$, but the variations are so wide that a realistic range is probably 220–300 $ohm^{-1}$ $cm^2$. $mole^{-1}$.

Very few data are available for 3 1 electrolytes If a pair of very low values [67] and some exceedingly high ones [166] (430–472 $ohm^{-1}$. $cm^2$. $mole^{-1}$) are excluded, an average of ~ 380 $ohm^{-1}.cm^2$ $mole^{-1}$ and a range of 340–420 $ohm^{-1}.cm^2.mole^{-1}$ is obtained Typical examples within this range are in refs 72 and 304.

For higher electrolyte types, the complexes of some cationic ligands $[ML^+_4](ClO_4)_6$ and $[ML^+_6](ClO_4)_8$ (M = Co, Ni, Cu, Zn, Cd, Pd; $L^+$ = β-aminoethyltrimethylammonium, γ-aminopropyltrimethylammonium) are more interesting in terms of the unusual ligand systems than for the $\Lambda_M$ values, although the latter are carefully discussed [303].

## *(iii) Complexes of selected systems*

Measurements for complexes of nitrogen donors are typified by the work of Crawford and Melson [67], and of Fowles and Willey [305] for $Sc^{III}$ and $Zr^{III}$ complexes of, for example, bipyridyl, *o*-phenanthroline. Studies of complexes of oxygen donors are mainly restricted to *N*-oxides, particularly heterocyclic *N*-oxides [109,306,307] and trimethylamine-*N*-oxide [300,308] though one other useful study [111] concerns the $\Lambda_M$–$c^{1/2}$ data for $[Ti(acac)_3][FeCl_4]$. For sulphur donors the study [296] of some dithiolenes has already been considered as a definitive work, and the study by Busch and co-workers [309] of some complexes $NiLX_2$ (L = a cyclic tetradentate NNSS ligand, X = $Br^-$, $I^-$, $CNS^-$) which includes the use of Onsager plots to define the complexes as 1·1 electrolytes is also important. Complexes of phosphorus and arsenic donors have been studied by Meek and co-workers [120,310], and lead to $\Lambda_M$ values in the suggested ranges, whereas other values for similar donors are rather lower [311,312].

Cotton and co-workers have used $\Lambda_M$ data in their studies of systems containing the $Re_2Cl_8{}^{2-}$, $Re_2Cl_9{}^-$, $Re_2Br_9{}^-$, $Re_2Cl_9{}^{2-}$, and $Re_2Br_9{}^{2-}$ anions [313,314], and to characterise complex halothallium systems [315]. For other haloanions see refs 316 and 317. Conductivity data have been reported for some nitrosyl [318] and carbonyl [319] complexes; the latter are believed to contain hydride bridges Greenwood and Travers [320] have considered some decaborane–Cd complexes, and values have been given for some unusual boron compounds [321]

## H. DIMETHYLFORMAMIDE

### *(i) General considerations*

Although considerable use has been made of this solvent for measuring the conductivity of coordination compounds, and data are available for some 200 complexes covering all the common electrolyte types, there have been many instances of interpretational problems. These arise chiefly from the strong donor capacity of dimethylformamide, which frequently leads to displacement of (anionic) ligands and change of electrolyte type The best example is probably for complexes of DMF itself with a number of lanthanide nitrates [322] These are formulated as $Ln(DMF)_4(NO_3)_3$, are non-conducting in nitromethane, but have $\Lambda_M$ corresponding to 1·1 electrolytes in DMF It is proposed that one nitrate group is displaced by a further molecule of DMF, the conducting species being $[Ln(DMF)_5(NO_3)_2]NO_3$. Curiously, the analogous dimethylsulphoxide complexes

$Ln(DMSO)_4(NO_3)_3$ ionise [323] in DMF as 2:1 electrolytes, presumably $[Ln(DMSO)_4(DMF)_2NO_3](NO_3)_2$, as do some γ-butyrolactam complexes [324].

*(ii) Acceptable $\Lambda_M$ ranges for various electrolyte types*

In most previous work, the reference values for 1:1 electrolytes have been taken from the data of Sears and co-workers [325,326] for a series of tetraalkylammonium halides and simple salts. At $10^{-3}$ *M* the $\Lambda_M$ values range from 72 to 90 $ohm^{-1}.cm^2.mole^{-1}$ with an average $\Lambda_M$ of 83 $ohm^{-1}$ $cm^2$ $mole^{-1}$. Other more recent values for non-complex salts include 88 $ohm^{-1}$ $cm^2.mole^{-1}$ for $(CH_3)_4NI$ at $10^{-3}$ *M* [18], 76 $ohm^{-1}.cm^2.mole^{-1}$ for $K[C(CN)_3]$ at $10^{-3}$ *M* [327], and 61 $ohm^{-1}$ $cm^2.mole^{-1}$ for $(C_2H_5)_4NCl$ at $10^{-2}$ *M* [57]. The range for 1:1 electrolytes has been variously quoted ($ohm^{-1}$ $cm^2$ $mole^{-1}$) as 70–90 [328], 60–90 [329], 70–80 [188], 55–75 [330], 55–80 [46], and 85 downwards [331]. An average value for all complexes at $10^{-3}$ *M* is ~ 78 $ohm^{-1}$ $cm^2.mole^{-1}$, and on the basis of this compilation a reasonable range is probably 65–90 $ohm^{-1}.cm^2.mole^{-1}$

TABLE 11

Summary of the expected $\Lambda_M$ ranges for complexes of different electrolyte types at $10^{-3}$ *M* in the common organic solvents ($ohm^{-1}$ $cm^2$ $mole^{-1}$)

| | *Electrolyte type* | | | |
|---|---|---|---|---|
| *Solvent* | *1:1* | *2:1* | *3:1* | *4:1* |
| Nitromethane | 75 – 95 | 150 – 180 | 220 – 260 | 290 – 330 |
| Nitrobenzene | 20 – 30 | 50 – 60 | 70 – 82 | 90 – 100 |
| Acetone | 100 – 140 | 160 – 200 | 270 ? | 360 ? |
| Acetonitrile | 120 – 160 | 220 – 300 | 340 – 420 | 500 ? |
| Dimethylformamide | 65 – 90 | 130 – 170 | 200 – 240 | 300 ? |
| Methanol | 80 – 115 | 160 – 220 | 290 – 350 ? | 450 ? |
| Ethanol | 35 – 45 | 70 – 90 | 120 ? | 160 ? |

For 2:1 electrolytes the following ranges ($ohm^{-1}.cm^2.mole^{-1}$) have been suggested. 110–150 [46], 135–175 [188,328], and 140–170 [331]. When values less than 120 and greater than 180 $ohm^{-1}.cm^2.mole^{-1}$ are ignored, the present data yield an average $\Lambda_M$ at $10^{-3}$ *M* of ~ 150 $ohm^{-1}.cm^2.mole^{-1}$, in excellent agreement with the reference value obtained by Farago et al. [332], and the first suggested range above is undoubtedly too low. For most purposes, a range of 130–170 $ohm^{-1}.cm^2.mole^{-1}$ is realistic, though for complexes containing the tetraphenylborate anion values of ~ 115 $ohm^{-1}.cm^2.mole^{-1}$ are frequently obtained [332].

Rather extended ranges have been suggested for 3:1 electrolytes: 200–260 [331], 180–240 [333], 200–260 [186], 200–250 [188], and 175–220 [46] $ohm^{-1}.cm^2.mole^{-1}$, respectively. However, the data considered in this review indicate that at $10^{-3}$ *M* 200–240

$ohm^{-1}$. $cm^2$. $mole^{-1}$ is satisfactory, with an average value of ~ 222 $ohm^{-1}$. $cm^2$. $mole^{-1}$. Nevertheless, attention is drawn to the data of Burmeister et al [166] who measured $\Lambda_M$ at $10^{-3}$ *M* for a range of lanthanide complexes $[(n\text{-}C_4H_9)_4N]_3[M(NCS)_6]$; they report 10 values in the range 341–440 (average 397 $ohm^{-1}$. $cm^2$. $mole^{-1}$), but these values are so far from other published data that they have not been included in the overall compilation.

There appear to be no unambiguous values for 4 1 electrolytes [46], though extrapolation suggests a value approaching 300 $ohm^{-1}$ $cm^2$ $mole^{-1}$ at $10^{-3}$ *M.*

Apart from the standard texts, particularly useful methods for the purification of DMF have been given by Sears et al. [325] and Headridge [7].

### (iii) Complexes of selected systems

Attention is drawn in this section chiefly to systems for which solvent interactions appear to be at a minimum, many such systems are complexes of nitrogen donors For non-heterocyclic donors, some typical data are contained in the work of Duff [334,335] on 2-methoxyaniline and benzene-1,4-diamine, whilst an example of simple heterocyclic donors is the $\Lambda$–$c^{1/2}$ study of some pyridine complexes [328] Sutton has measured $\Lambda_M$ values for a wide range of (usually) bidentate heterocyclic donors in DMF; typical examples are complexes of substituted phenanthrolines [333], 2-thioamidopyridine [329], and 2-acetamidopyridine [75] A good example of a mixed N–O donor is provided by the quadridentate ethylenediamine-bis-acetylacetone. This ligand gives lanthanide complexes $[LnL_2]X_3$ ($X = Cl^-$, $NO_3^-$, $SCN^-$) which are a valuable source of data for 3.1 electrolytes [192].

The other major source of $\Lambda_M$ data in DMF concerns oxygen donors, and particularly *N*-oxides An early and much-quoted example, which nevertheless contains several uncertainties arising through solvent interactions, concerns complexes of pyridine-*N*-oxide [331]; the most valuable data are for the perchlorato- and nitrato-complexes, typically $[CoL_6]X_2$. More recent examples include the complexes of 2,2′-bipyridyl-*N,N′*-dioxide [336,337], and *N,N*-dimethylethylenediamine-*N*-oxide [338]

Finally, attention should be drawn to the careful $\Lambda_M$–$c^{1/2}$ study of Westland and Pluscec [122], already mentioned for nitromethane, and to the compounds of the tricyanomethanide ion $[C(CN)_3]^-$ which although not complexes are very relevant to this tabulation [327]

## I METHANOL AND ETHANOL

### (i) Methanol

There have been relatively few examples of the use of methanol as a solvent for $\Lambda_M$ studies of complexes, data for less than 100 compounds of this type being available. Although the conductivity values are comparable with those for nitromethane it is only rarely that solvolytic and dissociative problems can be discounted

Reference values are available for several tetraalkylammonium and arsonium salts

[177,262,339–341], and for certain picrates [342], at $10^{-3}$ *M* concentrations, an average $\Lambda_M$ excluding the tetraphenylborates and picrates is 93 $ohm^{-1}.cm^2$ $mole^{-1}$. For those complexes measured, successive approximation leads to a value of 97 $ohm^{-1}.cm^2.mole^{-1}$, though roughly 1 in 3 values exceed this average by ± 20%, clearly showing the unreliability of this solvent for this purpose. A reasonable range is probably 80–115 $ohm^{-1}.cm^2.mole^{-1}$ for 1 1 electrolytes.

A comparable procedure for 2 1 electrolytes leads to a value of ~ 191 $ohm^{-1}$ $cm^2$ $mole^{-1}$, with a rather smaller number of high deviations than for 1 1 electrolytes, and a range of 160–220 $ohm^{-1}.cm^2.mole^{-1}$ is suggested.

Data for 3 1 electrolytes are scanty and rather conflicting The values measured by Sutton [54,343] give $\Lambda_M$ ~ 330 $ohm^{-1}$ $cm^2$ $mole^{-1}$ at $10^{-3}$ *M*, in reasonable agreement with other electrolyte types, whereas a value of 199 $ohm^{-1}$ $cm^2.mole^{-1}$ for $[Fe(en)_3]Cl_3$ has been quoted [344].

Other electrolyte types are represented by a value of 278 $ohm^{-1}.cm^2.mole^{-1}$ for a 4 1 system [344] (almost certainly anomalously low), and of 625 $ohm^{-1}.cm^2$ $mole^{-1}$ for $[CrL_3]_2(SO_4)_3$ In the latter case the ligand is 2-aminomethylpyridine [54].

In view of the relative unimportance of methanol as a solvent for conductivity purposes, a detailed discussion of $\Lambda_M$ values is not justified. For nitrogen donors, attention is drawn to the work of Sutton [54,343,346,349], and to the data of Robinson and Busch [347], these authors include a discussion of solvolysis problems A recent paper is that by Barbucci et al [341].

Typical papers on arsenic donors include those on complexes of diarsine [348,351], whilst for sulphur donors a valuable source of conductivity data is the study [262] of some substituted thiourea ligands.

### *(ii) Ethanol*

Conductivity data for complexes in this solvent are even more sparse than for methanol, since, in addition to the solvolysis problems noted for methanol, the $\Lambda_M$ values are roughly half those in methanol

For non-complex electrolytes of the 1.1 type, the definitive paper is that of Evans and Gardam [350]. At $c = 10^{-3}$ *M* an average $\Lambda_M$ of ~ 40 5 $ohm^{-1}.cm^2$ $mole^{-1}$ was obtained, compared with ~ 41.5 $ohm^{-1}.cm^2.mole^{-1}$ for the (thirteen) complexes on which an average was calculated A previously suggested [351] range of 35–45 $ohm^{-1}$ $cm^2$ $mole^{-1}$ is thus reasonable.

For 2.1 electrolytes an average value of ~ 77 5 $ohm^{-1}.cm^2.mole^{-1}$ is obtained, and a suggested range is 70–90 $ohm^{-1}$ $cm^2$ $mole^{-1}$.

The three values [150] for 3 1 electrolytes give $\Lambda_M$ ~ 121 $ohm^{-1}.cm^2$ $mole^{-1}$, though a value of 380 $ohm^{-1}$ $cm^2.mole^{-1}$ has been quoted [352].

The bulk of the conductivity data for complexes in ethanol derive from the work of Sutton [150,248,353]

J MISCELLANEOUS SOLVENTS

*(i) Dimethylsulphoxide*

The standard paper on the conductivity of non-complex 1.1 electrolytes in this solvent is that of Sears et al [354]. An approximate $\Lambda_M$ at $10^{-3}$ $M$ for the solutes given is 35 ohm$^{-1}$. cm$^2$. mole$^{-1}$, with individual values ranging from ~ 23 (potassium octadecylsulphate) to 42 ohm$^{-1}$. cm$^2$. mole$^{-1}$ (potassium thiocyanate) Values published [355] for complexes $[MCl_2(en)_2]Cl$ (M = Ru, Co) also fall into this range. A value of 37 8 ohm$^{-1}$ cm$^2$. mole$^{-1}$ published [24] for $[(C_6H_5)_4P]NO_3$ also supports this range, and is in contrast to the value of 73 2 ohm$^{-1}$ cm$^2$ mole$^{-1}$ for the corresponding hydrogen dinitrate salt $[NO_2OHONO_2]^-$. It may also be noted that Greenwood et al. have suggested 50—70 ohm$^{-1}$. cm$^2$. mole$^{-1}$ as the range for 1.1 electrolytes in DMSO [356].

Data over a concentration range have been published by Allen et al [357], including the nitrogen complex $[Ru(NH_3)_5N_2]I_2$, but the concentration range used ($10^{-4}$—$10^{-5}$ $M$) makes direct comparison with the values at $10^{-3}$ $M$ difficult

It should also be noted that another complex formulated as containing molecular nitrogen, $[Ru(en)_2(H_2O)N_2][B(C_6H_5)_4]_2$, has been investigated in DMSO [358] The $\Lambda_M$ value of 35 ohm$^{-1}$ cm$^2$. mole$^{-1}$ is exactly the value for standard 1.1 electrolytes, but could be explained by the low ionic mobility of tetraphenylborate noted earlier

The only data for complexes of the 3·1 electrolyte type in DMSO concern the complexes of DMSO itself, $[Ln(DMSO)_n(NO_3)_3]$, ($n$ = 3,4; Ln = La, Ce, Pr, Nd, Sm, Gd, Y, Ho, Yb) [323]. The average $\Lambda_M$ of 109 ohm$^{-1}$ cm$^2$ mole$^{-1}$ seems reasonable in relation to the 1 1 complex electrolytes, and the authors quote previous work [359] in support of this value.

*(ii) Nitroethane*

Data for this solvent have been published almost exclusively by various groups of Italian workers (see, for example, refs 164, 174, 360—362) Data for non-complex 1 1 reference electrolytes [174,361,363,364] suggest a value of 70 ohm$^{-1}$ cm$^2$. mole$^{-1}$, though the average value for those complexes which have been measured (e.g refs 164, 361) suggest a value of 80 ohm$^{-1}$. cm$^2$. mole$^{-1}$, a range of 65—95 ohm$^{-1}$. cm$^2$. mole$^{-1}$ seems reasonable. There is a particularly valuable example [360] of the reduction in $\Lambda_M$ values with the tetraphenylborate anion, in this case to ~ 50 ohm$^{-1}$. cm$^2$. mole$^{-1}$.

Complexes of the 2·1 electrolyte type have not been widely studied, but the most reliable values appear to be 147 ohm$^{-1}$. cm$^2$. mole$^{-1}$ for $[(C_2H_5)_4N]_2[Co(CNS)_4]$ [164], and 125 ohm$^{-1}$. cm$^2$. mole$^{-1}$ for $[(n\text{-}C_4H_9)_4N]_2[NiBr_4]$ [362]. The discussion of the use of the Van't Hoff coefficient for distinguishing electrolyte types is also of importance [164] For other data in nitroethane see ref. 365.

*(iii) 1,2-Dichloroethane*

This solvent has been used occasionally for $\Lambda_M$ determinations on complexes, but the low values obtained relative to other solvents do not commend its use. The most reliable reference value [363,366], for $[(n\text{-}C_4H_9)_4N]Br$, is 19.0 $ohm^{-1}.cm^2.mole^{-1}$, and is supported by the values obtained [360,363] for 41 complexes in the range 10–24 $ohm^{-1}.cm^2.mole^{-1}$ (average 18.2 $ohm^{-1}$ $cm^2$ $mole^{-1}$). Similar values have been published more recently [83] for some complexes of multidentate N donors, but higher values were obtained for some acetylacetonates [367] and some $Pt^{II}$–phosphine complexes [368].

The use of the related solvent dichloromethane has been criticised by Rosenthal and Drago [55], though there is at least one example [369] of an apparently successful use in this solvent.

### *(iv) Dimethylacetamide*

This solvent has been used by Madan and co-workers [370,371] for investigation of complexes of the solvent itself; they suggest the following ranges for the various electrolyte types ($ohm^{-1}$ $cm^2.mole^{-1}$), 1.1, 85 downwards, 2.1, 130–180; 3·1, 200–250. The value for 2 1 electrolytes is supported [372] by nine values for complexes also of DMA itself, $[Ln(DMA)_4(ReO_4)_3]$, formulated as $[Ln(DMA)_4(ReO_4)](ReO_4)_2$ in solution.

### *(v) N-methylpyrrolidone*

The use of this solvent has been suggested recently, and some conductivity data presented by Nyholm and co-workers [373]

## K TOXICITY OF SOLVENTS

Attention should be drawn to possible harmful effects of the solvents considered in this Review, particularly through respiratory or skin absorption. Although this need not be an over-riding consideration it may nevertheless affect the convenience of experimental determinations, particularly for the more toxic reagents. A widely used source of information is the Laboratory Handbook of Toxic Reagents (The Royal Institute of Chemistry, C.H. Gray (Ed.)), which lists the following threshold limit values (p.p.m.): nitrobenzene, 1; dimethylformamide, 20; acetonotrile, 40, dichloroethane, 50, nitroethane, 100; dichloromethane, 500. A similar compilation published in chart form by B.D.H. Ltd, lists a value of 1000 p.p m. for acetone. Values do not appear to be readily available for nitromethane or dimethylsulphoxide; it is likely that the value for the former would be at least as great as for nitroethane (i e. $\geqslant$ 100 p p m ), but for dimethylsulphoxide it could well be less than this value.

It is clear from these toxicity values that usage of nitrobenzene should be strictly limited, and they may also be considered to oppose the use of dimethylformamide and acetonitrile.

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