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

SOLVENT COORDINATION NUMBERS OF METAL IONS IN SOLUTION

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(Received July 21st, 1970)

CONTENTS

ABBREVIATIONS

acac	acetylacetonate (2,4-pentanedione)	ID	isotopic dilution
dmso	dimethylsulphoxide	PMR	proton magnetic resonance
dmf	*N,N'*-dimethylformamide	NMR	nuclear magnetic resonance
CN	number of solvent molecules in the first coordination sphere of a metal ion in solution	ppm	parts per million
		RDF	radial distribution function

A. INTRODUCTION

The association of solvent molecules with metal ions in solution has intrigued chemists for at least the last fifty years, and is currently the subject of much research. Of particular significance in the early publications were the largely electrostatically based models proposed by Garrick[1,2] and Bernal and Fowler[3], which greatly reinforced the idea that a small and definite number of solvent molecules compose the first solvation sphere of a metal ion in solution. Since that time no other major theories predicting solvation numbers have been published, but numerous experimental solvation number studies, in which a wide range of techniques have been employed, have appeared in the literature

The solvated metal ion in a large number of cases is a molecular species, as has been demonstrated, for example, by solvent exchange and ligand substitution studies[4-6]. The solvated metal ion is the most ubiquitous of all metal complexes and, in consequence of this, the exact composition of its first coordination sphere is of considerable interest. The purpose of this review is (*1*) to examine the methods by which the numbers of solvent molecules in the first coordination sphere of metal ions in solution (henceforth abbreviated CN) have been determined, (*2*) to review the results obtained and the incidental additional data on other aspects of metal ion solvation associated with these results, and (*3*) to outline the significance of this area of metal-complex research endeavour to related areas of investigation

B EXPERIMENTAL METHODS

(i) General remarks

At this point it is important to consider how the term "first coordination sphere" might be defined for a solvated metal ion. Probably the most obvious definition is one in which only molecules in "contact" or "bonding" distance of the metal ion, such that no other solvent molecules are interposed between them and the metal ion, are considered to compose the first coordination sphere Such a *time-independent* definition is, of course, applicable to an arrangement of solvent molecules around a metal ion arising solely from packing requirements and does not meet completely the description of the molecular entity, which metal complexes are conventionally considered to be Clearly a complementary *time-dependent* definition of the first coordination sphere is also required if specific solvent–metal ion interactions are to be accounted for. In general terms, then, a solvent molecule in the first coordination sphere might be defined as one having a residence time in the immediate vicinity of the metal ion, long by comparison to its correlation time in subsequent solvation spheres and the bulk solvent. (From this point "bulk" solvent will be taken to include all solvent molecules not in the first coordination sphere.) Obviously the solvent residence time will vary with the lability of the metal ion, and consequently in the case of the more labile metal ions[5], e g. Cs^+, Rb^+, K^+, Ba^{2+}, Hg^{2+}, this time-dependent definition may be of marginal value only.

The preceding discussion indicates that, in principle, there are two types of methods by which CN may be determined

(*1*) the first method distinguishes solvent molecules on the basis of their distance from the metal ion, and the number of solvent molecules within contact distance of the metal ion is equated to CN. Depending upon the lability of the metal ion the CN determination may be made over a fraction of a solvent exchange half-life or over many such half-lives Such a method is time-independent and is exemplified by the X-ray diffraction method.

(*2*) The second method utilises the fact that in many cases the residence time of a solvent molecule in the first coordination sphere of a metal ion is significantly longer than its correlation time in the bulk solvent, to distinguish between solvent molecules in these two environments Obviously the time elapsed in making such a distinction will critically determine the suitability of a given method for determining CN values for metal ions. A number of such time-dependent methods, applicable over differing ranges of metal ion lability, have been developed, e g isotopic dilution, ion exchange separation and chemical analysis, NMR area methods and one NMR shift method

It should be noted that both of the above general methods in principle observe the solvent molecules in the first coordination sphere directly, and hence may be collectively termed *direct* methods. In addition to these methods, others, which will be termed *indirect* methods by virtue of the fact that they do not directly observe solvent molecules in the first coordination sphere, have been used to determine "solvation numbers" of metal ions in solution, and are discussed below under "Indirect methods"

(ii) X-Ray diffraction

X-ray diffraction in principle offers a method of measuring mean solute–solvent interaction distances and intensities. The measurement of intensities of X-rays diffracted by a salt solution, and the bulk density of that solution facilitates the determination of the radial distribution function[7] (RDF). $4\pi r^2 \rho(r)$, which gives the number of atoms in a spherical shell of unit thickness centred on a selected atom In the event that specific solute–solvent interactions exist in solution the observed RDF exhibits peaks appearing at mean solute–solvent contact distances, in contrast to the smooth parabola expected for the RDF of a uniform liquid. In practice, pure solvents, e g water, methanol, ethanol[8–9], exhibit peaks in their RDF curves which are attributed to specific intermolecular interactions. In some cases these peaks coincide with peaks attributed to solute–solvent interactions and thereby lead to uncertainty in the interpretation of the RDF curves of some salt solutions[10].

In recent investigations of concentrated Co^{2+} solutions Kruh et al.[11–12] have used a relationship in which a peak area in the RDF may be correlated with the average number of atoms of type j around atom i in solution by the expression

$$A_{ij} \simeq \chi_i \sigma_n Z_i Z_j$$

where A_{ij} denotes observed peak area, Z_i and Z_j are atomic numbers, σ is a counting factor and equals 2 for unlike atoms, and n represents the average number of atom pair interactions at r_{ij}, the average interaction distance for the peak considered. From the above expression it is apparent that observed and calculated peak areas together yield n.

In the RDF (Fig 1) of an aqueous solution of $CoBr_2$, Wertz and Kruh[12] identified a broad maximum centred at ca. 2.1 Å as due to cobalt–oxygen interaction. The observed peak area was ca. 2560 $(e^-)^2$ and the calculated area per cobalt–oxygen contact was ca. 435 $(e^-)^2$ thus indicating that $Co(H_2O)_6{}^{2+}$ was the predominant species in solution. A second peak at 3.25 Å was attributed to oxygen–bromine interactions. Similarly in aqueous $CoCl_2$ solution $Co(H_2O)_6{}^{2+}$ was found to be the predominant species with cobalt–oxygen and oxygen–chlorine interaction distances of ca. 2.1 Å and 3.1 Å, respectively[11]. In methanol solutions of $CoBr_2$ the major species was found to be $CoBr_2(CH_3OH)_2$ with cobalt–oxygen and cobalt–bromine interaction distances of 2 00 Å

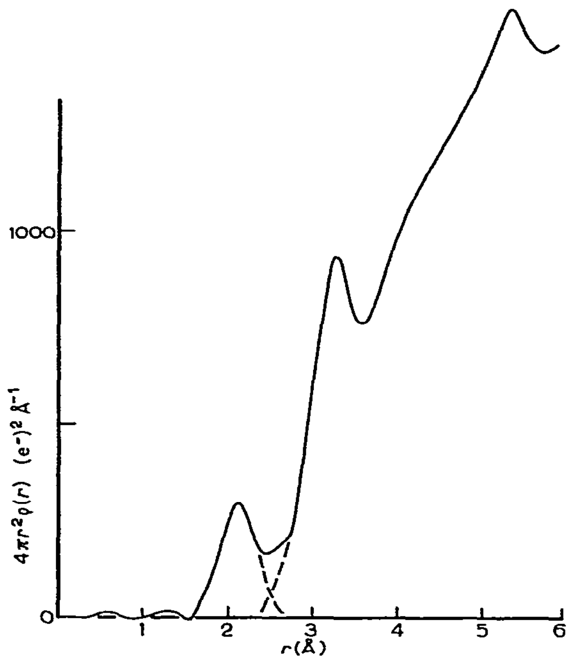

Fig 1 RDF of an aqueous $CoBr_2$ solution Broken lines indicate graphical resolution (after Fig 2, Ref 12)

and 2.45 Å respectively In contrast a highly associated species, $(CoCl_2)_n$, in which Cl^- occupied the first coordination sphere in tetrahedral array, with cobalt–chloride interaction distances of 2.30 Å, predominated in ethanol and methanol solutions of $CoCl_2$ It is of interest to note that evidence for such a polymeric species has also been obtained from molecular weight measurements[13] of $CoCl_2$ in solvents of low dielectric constant, and also from mass spectral studies of $CoCl_2$ vapour[14].

In earlier applications of the X-ray method Brady and Krause[15,16] determined CN for K^+ to be 4 in aqueous KOH solution. The potassium–oxygen interaction distance varied between 2.87 Å and 2.92 Å depending upon salt concentration They were unable to obtain directly a CN value for Li^+ due to the small X-ray scattering by that ion. The CN for aqueous solutions of $ErCl_3$ and ErI_3 was found to be 6 with erbium–oxygen interaction distances of 2.3 Å in both cases[17]. In addition, well-defined solvent separated ion pairing between $Er(H_2O)_6{}^{3+}$ and two chlorides or two iodides was identified with erbium–chloride and erbium–iodide interaction distances of 4.6 Å and 5.4 Å respectively. In aqueous solutions of $FeCl_3$ in the concentration range, 1.5–5.0 M no aquated Fe^{3+} species were unambiguously identified, but the species $FeCl_6{}^{3-}$ and Fe_2Cl_6 were identified as major species at the higher and lower extremes of the concentration range, respectively[18] The identification of species in this latter study has been subjected to some criticism[10]

It is apparent from the above data that the X-ray method not only provides a means for CN determination, but also, within the limitations of a unidimensional approach, yields structural information.

(iii) Isotopic dilution

Isotopic dilution methods depend upon the statistical distribution of an isotopically labelled solvent throughout the system studied, such that in a solution containing metal ions CN values may be derived via the equality

$$\frac{\text{concentration of isotopically labelled solvent in coordinated solvent}}{\text{concentration of isotopically labelled solvent in bulk solvent}} = \frac{\text{number of coordinated solvent molecules}}{\text{number of bulk solvent molecules}}$$

Isotopic fractionation effects must, of course, be allowed for in the above equality, but usually the mass of a solvent molecule is large by comparison to isotopic mass differences and hence these effects are small

A major limitation of the isotopic dilution technique that the half-life for solvent exchange on the metal ion must be long compared to isotopic sampling time. Also the clean separation of coordinated and bulk solvent, prior to isotopic assay is of crucial importance.

The first application of this technique was reported by Hunt and Taube[19] who determined the CN of Cr^{3+} to be 6 2 ± 0 2 in water via an ^{18}O isotopic dilution (ID) method. An acidic solution of $Cr(ClO_4)_3$ in water of normal isotopic abundance was mixed with ^{18}O enriched water. Bulk water was distilled off in vacuo at time intervals and was analysed mass spectrographically via a CO_2 equilibration method. The CN for Cr^{3+} was calculated from the infinite time value ($t_{1/2}$ for solvent exchange ca 40 h at 25°C) for the ^{18}O content of the bulk water. Similar methods have been employed to determine the CN values of Al^{3+} and Rh^{3+} in water[20,21] and of Cr^{3+} in ammonia[22], and in each case values close to 6 were obtained Isotopic dilution investigations of Li^+, Cd^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+} and Pr^{3+} in methanol using ^{18}O-labelled methanol at low temperatures have been reported[23,24]. The rapidity of solvent exchange on Li^+ and Cd^{2+} proved too great to permit CN determinations In the case of Mg^{2+}, Co^{2+} and Ni^{2+} a range of CN values for methanol was reported for each cation It was considered that the trend in the observed CN values was consistent with an actual CN value of 6, and further that the observed CN deviation from this value was due to trace amounts of water in the solvent which competed effectively with methanol for coordination sites This was confirmed by a PMR study of the Mg^{2+} system[25] For the Fe^{3+} and Pr^{3+} ion a kinetically distinguishable first coordination sphere was detected, but, particularly in the case of Fe^{3+}, it appeared that interaction with anions precluded the determination of an unambiguous CN value.

In addition to the investigation of cations solvated by a single solvent, the isotopic dilution technique has also been used to establish the aquo and diaquo formulae of $Co(NH_3)_5(H_2O)^{3+}$ and $Co(NH_3)_4(H_2O)_2{}^{3+}$, respectively, in aqueous solution[26,27].

(iv) Ion exchange separation and chemical analysis

The slow solvent exchange rates of Cr^{3+} solvento complexes in which more than one solvent may jointly occupy the first coordination sphere permits the separation of the Cr^{3+} solvento complexes intact, on a cation exchange resin column, from an equilibrated system. For a number[28-33] of such systems gradient elution has been used to remove all of the Cr^{3+} solvento complexes in separate fractions from the resin Analysis of each eluent fraction for Cr^{3+} and coordinated solvent facilitates precise identification of the constituents of the first coordination sphere of each Cr^{3+} solvento complex In a typical study King et al [28] identified all of the complexes $Cr(OH_2)_{6-n}(dmso)_n{}^{3+}$ in the aqueous dmso system In Fig 2 an elution pattern for an aqueous dmso solution of $Cr(ClO_4)_3$ is shown It may be seen that in some cases geometric isomers are indicated by the appearance of two eluent fractions corresponding to identical H_2O dmso mole fraction ratios in the first coordination sphere of Cr^{3+}.

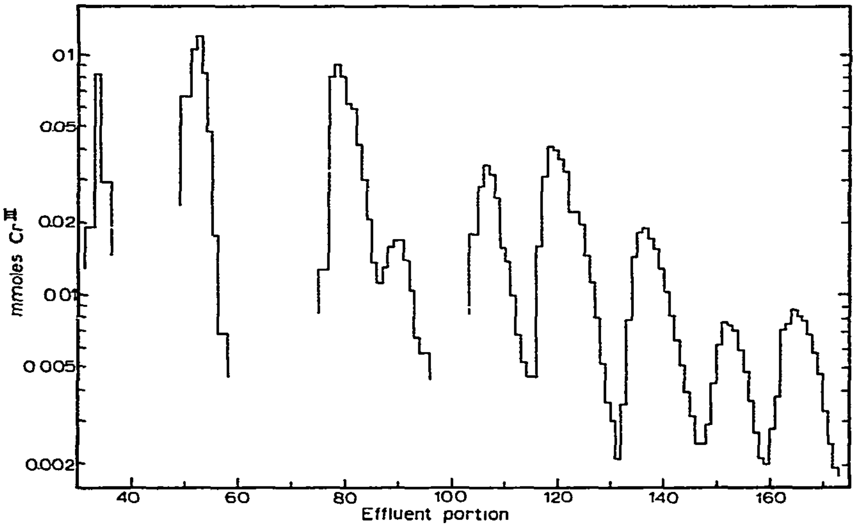

Fig 2. Elution separation of species $Cr(OH_2)_{6-n}(dmso)_n{}^{3+}$, from a solution in which the mole fraction of dmso was 0.095 The values of the mean number of dmso molecules in the first coordination sphere $\bar{n}$ for ca. 7 ml portions of effluent are 33 (single portion), 0.00, 51–55, 1.00, 77–81, 2.03, 88–91, 2.08, 105–108, 2.97, 118–121, 2.96, 135–138, 3.88, 150–155, 4.87, and 162–167, 3.93. Gradient elution: 1.5–6 M H_2SO_4, Dowex 50W-X4 200–400 mesh (after Fig. 2, Ref. 28).

(v) Nuclear magnetic resonance – area method

A nucleus ($I \neq 0$) in different bonding environments exhibits separate resonances, corresponding to each such environment, over a frequency range. In the event that interchange between two such environments occurs, two distinct resonances are observed in the slow exchange limit and these coalesce to a single time averaged resonance in the fast exchange limit[34]. This phenomenon has been exploited to a considerable extent in the determination of metal ion CN values in solution.

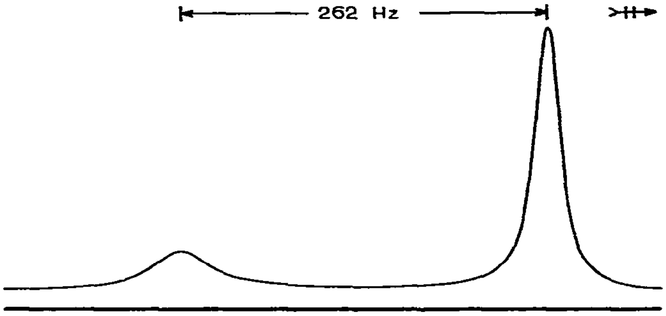

Fig 3. PMR spectrum of a 2 1 M aqueous solution of $Al(NO_3)_3$ at −40°C The low field resonance arises from the coordinated solvent, and the high field resonance from the bulk solvent (after Fig 1, Ref 35)

Under conditions where separate resonances are observed for solvent molecules in the first coordination sphere of a metal ion, and in the bulk solvent, direct integration of, and subsequent comparison of, the areas under the two resonances, combined with a knowledge of the metal ion concentration, yields the metal ion CN In this way the CN of Al^{3+} has been determined to be 6 in a number of solvents A typical PMR spectrum[35] is shown in Fig 3 for an aqueous solution of $Al(NO_3)_3$. It is usually assumed in this method that solvent in environments other than the first coordination sphere are exchanging at diffusion-controlled rates and therefore appear in the environmentally averaged bulk solvent resonance Frequently, the rate of solvent exchange, and the chemical shift between the first coordination sphere and the bulk solvent, is such that separate resonances are only observed when the solvent exchange rate is slowed by cooling. An additional problem encountered in aqueous PMR studies is that rapid proton exchange on coordinated water leads to environmental averaging of the proton resonance Fratiello et al.[36] have demonstrated that not only does acetone slow down the rate of proton exchange and depress the freezing point of such aqueous solutions without causing precipitation of the metal salt, but also that acetone acts as an inert diluent.

The PMR area method has also been used in binary solvent systems, e g Mg^{2+} in aqueous methanol[25], and Al^{3+} in aqueous dmso[37–39]; and coordinated and bulk resonances have been observed for both solvents from which total CN values close to 6 have been calculated Matwiyoff et al. have employed this method in studies of the Be^{2+}, Al^{3+} and Ga^{3+} mixed complexes of dmf and 2,4-pentadione in dmf solvent[40–42] From resonances arising from dmf and 2,4-pentadione a total CN value of 4 was calculated for Be^{2+} and the mono- and bis-(2,4-pentadionato) species were identified Similarly a total CN of 6 was obtained for Al^{3+} and Ga^{3+} and mono-, bis-, and tris-(2,4-pentadionato) species were identified in both systems together with cis- and trans-$Al(acac)_2(dmf)_2$ The use of this method in identifying isomers of complexes in which no solvent is coordinated is well documented[43,44]

Studies of aqueous diamagnetic systems via ^{17}O NMR show that considerable overlap occurs between the resonances arising from coordinated and bulk water. Jackson et al [45] overcame this problem by addition of labile and paramagnetic metal ions such as Dy^{3+},

Cu^{2+} and Co^{2+} to solutions of diamagnetic metal salts with the result that the bulk ^{17}O resonance was either broadened or shifted to such an extent that the resonance arising from water coordinated to the diamagnetic metal ions was separately observed. In this way CN values close to 4, 6 and 6, respectively were obtained for Be^{2+}, Al^{3+}, and Ga^{3+} in water[46,47]. This method has also been applied to the ^{14}N NMR determination of a CN value close to 6 for Al^{3+} in liquid ammonia[48].

(vi) Nuclear magnetic resonance – shift method

Exchange of solvent on a paramagnetic metal ion such as Dy^{3+} at rates at which complete environmental averaging occurs frequently results in a single resonance being observed for the solvent nucleus at a frequency greatly shifted (10^2–10^3 ppm) from that of the pure solvent This solvent shift is directly proportional to the paramagnetic ion concentration (any shift induced by the anion is relatively negligible) and also to the number of coordination sites, and inversely proportional to the solvent concentration. In a solution containing a second metal ion on which the rate of solvent exchange is significantly less than that on Dy^{3+} those solvent molecules in the first coordination sphere of the second ion are effectively removed from the environmental averaging process and hence the Dy^{3+} induced solvent shift is increased such that

$$\delta m'_{\text{solvent}}/m'_{Dy^{3+}} = \delta^0 m^0_{\text{solvent}}/m^0_{Dy^{3+}}$$

where m_x represents the millimoles of species x in solution, and the superscript 0 denotes the quantity measured in the solution containing only Dy^{3+} The only unknown is m'_{solvent}, the number of millimoles of environmentally averaged solvent in the solution containing the second metal ion Subtraction of m'_{solvent} from the known total number of millimoles of the solvent in this solution and division by the known number of millimoles of the second metal ion yields CN for the second metal ion Utilising this method Alei and Jackson[49] determined CN for Al^{3+} and Be^{2+} in water to be 5 9 and 3.9, respectively Application of this method to relatively inert Cr^{3+} is apparently complicated by the paramagnetism of this ion[49]. A particularly interesting result[50] was obtained when this method was applied to aqueous solutions of $VOSO_4$. Dysprosium (III) was employed to induce a shift of the bulk water ^{17}O resonance, and a CN value of 3 8 ± 0.2 was obtained This result was rationalised in terms of the species $VO(H_2O)_5{}^{2+}$ possessing four equatorial water molecules each with a residence time τ_m of 1.35×10^{-3} sec^{-1} at 300°K, and one equatorial water molecule, trans to the vanadyl oxygen, and of sufficient lability ($\tau_m \sim 10^{-11}$ sec^{-1} at 300°K) to undergo complete environmental averaging with bulk solvent and hence make no contribution to the observed CN value.

As δ is proportional to the number of coordination sites on the labile paramagnetic metal ion, occupation of such a site by another species leads to a decrease in δ, providing the solvent isotropic shift, $\Delta\nu_m$, remains constant, and hence the number of sites so occupied may be calculated via the expression:

$$\delta = [M][\text{solvent}]^{-1} q\Delta\nu_m$$

where q is the number of solvent molecules in the first coordination sphere of the metal M. Luz and Shulman[51] used this method to determine that only a single phosphate group of RNA coordinates to Co^{2+} in aqueous solution[51], and in an earlier study McDonal and Phillips[52] investigated the coordination of histidine to Co^{2+}. A limitation on the applicability of this method is that $\Delta\nu_m$ may vary considerably with q as has been demonstrated in the case of Co^{2+} by Horrocks and Hutchison[53].

(vii) Indirect methods

The direct methods each measure quantitatively a phenomenon closely identified with solvent in the first coordination sphere, such that a definite mole fraction of the solvent of a solution under investigation may be assigned to the first coordination sphere of the metal ion in that solution. In contrast the indirect methods usually measure a bulk phenomenon, i e. a phenomenon emanating from solute–solvent, and solvent–solvent interactions other than, and in addition to, the interactions between the metal ion and its first coordination sphere. Although these indirect methods yield quantitative measurements the "solvation numbers" derived from them are often very dependent upon the model used in the derivation, and frequently appear to include solvent outside the first coordination sphere. A consequence of this is that the "solvation number" for a given metal ion may vary with the method employed, e g values derived for Al^{3+} from entropy[54], compressibility[54] and proton relaxation time measurements[55] are 21, 31 and 16, respectively It is apparent that such "solvation numbers" do not correspond to the strictly defined CN which is the subject of this review. Nevertheless much valuable insight into the solvation of ions and solvent structure has been gained via the indirect methods, and for further reading in these areas the reader is directed to recent reviews[54,56–59] which discuss a number of indirect methods not considered here

An indirect method which differs appreciably from the class mentioned in the preceding paragraph in that the quantity measured, namely the metal-ion absorption spectrum, is mainly affected by the immediate environment of the metal ion, is particularly relevant to this review. The absorption spectra of transition metal ions arising from d–d electronic transitions are sensitive to the immediate environment of the metal ion, and are interpretable in terms of the geometry of this environment via crystal field and ligand field theory. Thus Ni^{2+} in a tetrahedral environment in a ZnO matrix exhibits bands at 15,100, 16,000 and 17,400 cm^{-1}, whereas in an octahedral environment in a MgO matrix bands are observed at 15,000, 22,000 and 24,000 cm^{-1}. The latter spectrum is very similar to that of $Ni(H_2O)_6{}^{2+}$ in the solid state and to that of Ni^{2+} in aqueous solution, from which it was concluded that regular octahedral $Ni(H_2O)_6{}^{2+}$ predominates in aqueous solution[59–62]. Via this rationale the ions[62–70] Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+} were also shown to have regular octahedral environments in aqueous solution inferring the general formula $M(H_2O)_6{}^{m+}$. (The ions Cr^{3+}, Co^{2+} and Ni^{2+} have been shown to have CN values close to 6 via direct methods as seen in Table 1.) From the absorption spectra of aqueous solutions of Cu^{2+} and V^{4+} it was concluded that both ions were hexacoordinated, but tetragonally distorted[10,71,72] with formulae $Cu(H_2O)_6{}^{2+}$ and $VO(H_2O)_5{}^{2+}$, respectively. From ^{17}O NMR solvent exchange experiments[73] evidence has been adduced for tetragonal distortion in $Cu(H_2O)_6{}^{2+}$ and ^{17}O NMR experiments have also given strong support for the formulation of $VO(H_2O)_5{}^{2+}$ in aqueous solution[50] It is apparent that CN predictions via absorption spectra of the first row transition ions correlate well with CN values determined via other methods. This method has been extended beyond the first row transition series and has been reviewed by Taube[10]. The more general utilisation of absorption spectra in equilibrium and kinetic studies of transition metal ions in solution is well known

C. SOLVENT MOLECULES IN THE FIRST COORDINATION SPHERE – EXPERIMENTAL RESULTS

The majority of the CN values obtained in single-solvent systems up to mid 1970 are listed in Table 1. It is seen that CN ranges from ca. 4 for Be^{2+} to 9.1 for Th^{4+}, although the majority of the values so far reported are close to 6 The Al^{3+} ion, probably because of its relatively slow solvent exchange rate and the ease with which its salts are handled, has been subjected to the greatest number of CN studies. It is noteworthy that three different NMR methods and an ^{18}O isotopic dilution technique all yield CN values close to 6 for Al^{3+} in water A CN value of 6 is also observed for Al^{3+} in several other single solvents and also in mixed solvents (section D), and deviations from this value are usually attributable to contact ion pairing (section E)

The only tetrahedral species detected by CN studies appear to be $Be(H_2O)_4{}^{2+}$(Refs 46,49) and $Be(dmf)_4{}^{2+}$ (Ref 40). Two other tetrahedral species $Co(H_2O)_4{}^{2+}$, postulated from ^{17}O NMR line-broadening[73], and temperature-jump[74] studies, and $Zn(H_2O)_4{}^{2+}$, postulated from temperature-jump studies[74], have not been detected, but CN values close to 6 have been obtained for both Co^{2+} and Zn^{2+} in water[11,12,75,76]. This result is in agreement with the postulated[74] low concentrations of the tetrahedral species relative to their octahedral analogues.

Only two CN values of 5 have been reported The first case was for Mg^{2+} in liquid ammonia, but later investigations[77] show this value to be in error and a value of 5.9 ± 0.1 is now reported. This result is consistent with values close to 6 observed for Mg^{2+} in H_2O[78,79,25], CH_3OH[80,81,25] and C_2H_5OH[82] A CN value of 5.1 is observed for Sc^{3+} in water, but Fratiello et al [75] consider that this value may be low due to contact ion pairing with nitrate ion.

At present there appears to be no evidence for CN variation over quite considerable temperature ranges[76] as may be seen in Table 1. Variation of CN with concentration has been observed in the $Zn(ClO_4)_2$–methanol[83] system, but this has been attributed to the formation of contact ion pairs rather than a change in the total coordination number of Zn^{2+}.

All the CN data so far available have been obtained from concentrated solutions of metal salts (usually greater than 0.1 *M* salt concentration), and this raises the question of the validity of such CN values in dilute solution Although there is no direct answer to this question it is noteworthy that weakly coordinating acetone is observed to enter the first coordination sphere of Al^{3+} in aqueous acetone solutions when the mole fraction ratio $H_2O{\cdot}Al^{3+}$ falls below 6 such that the Al^{3+} total coordination number remains close to 6[38]. It appears reasonably to assume from this that the CN value of 6 exhibited by Al^{3+} at $H_2O.Al^{3+}$ greater than 6, when only water coordinates, is the maximum CN

TABLE I

Experimental CN values for the coordination of a single solvent

Cation[a]	Solvent[b]	CN[c]	Temp (°C)[d]	Method[e]	Ref
Al^{3+}					
$Al(ClO_4)_3$	H_2O	6 0	-50	PMR (a)	78
		6 0^{f}	-35– -52	PMR (a)	75
		6.1–5.9	20	^{17}O NMR (s)	49
	dmf	6 0±1	37	PMR (a)	124
		6 0±0 3	0– -80	PMR (a)	117
	dmso	5.96–5 81	20– 40	PMR (a)	127
$Al(NO_3)_3$	H_2O	6±0 5	23	^{18}O ID	20
		6 01±0 02	-30– -55	PMR (a)	35
		6 0	-40	PMR (a)	78
$AlCl_3$	H_2O	6 1±0 1	-29 5	PMR (a)	125
		6 0	-47	PMR (a)	78
		6 0^{f}	-20– -40	PMR (a)	37
		6.0–6.1	-47	PMR (a)	126
		6.07–5.82	35	^{17}O NMR (a)	46
	dmf	6 0±0 1	37	PMR (a)	124
		5 7±0 3	0	PMR (a)	116
$AlBr_3$	H_2O	5.6–5.9	54– -62	PMR (a)	78
	dmf	5 7±0 3	20	PMR (a)	116
		6 0±0 1	37	PMR (a)	124
AlI_3	dmf	6 0±0 1	37	PMR (a)	124
		5 7±0 3	20	PMR (a)	116
	NH_3	6 03±0 45	27	^{14}N NMR (a)	48
Be^{2+}					
$Be(ClO_4)_2$	H_2O	3.7–3.9	20	^{17}O NMR (s)	49
Be	dmf	3.98–4.23	0– -40	PMR (a)	40
$BeCl_2$	H_2O	4.0–4.5	-20– -62	PMR (a)	78
Be	H_2O	3.95–4.30	18– 32.7	^{17}O NMR (a)	46
Co^{2+}					
$Co(ClO_4)_2$	H_2O	5.9±0 3	-38– -63.7	PMR (a)	76
	CH_3OH	5 8	-60	PMR (a)	100
	dmf	5 8±0 3 6 0±0.1	-45– -70	PMR (a)	86
	CH_3CN	5 7±0 3	-35– -45	PMR (a)	85
$CoCl_2$	H_2O	6	ambient	X-ray	11
$CoBr_2$	H_2O	6	ambient	X-ray	12
$^{g}Co^{2+}$	dmso	6 0±0 2	h	PMR (a)	128
Ga^{3+}					
$Ga(ClO_4)_3$	H_2O	6 28±0 26	35	^{17}O NMR (s)	129
		5 89±0 20	35	^{17}O NMR (a)	129
		5 9±0 4	h	^{17}O NMR (a)	89
		5.9–6.1	-35– -75	PMR (a)	78

TABLE I (*continued*)

Cation[a]	Solvent[b]	CN[c]	Temp (°C)[d]	Method[e]	Ref
$Ga(ClO_4)_3$	dmf	5 9±0 1	0–20	PMR (a)	42
$Ga(NO_3)_3$	H_2O	5 9±0 1	25	^{17}O NMR (a)	130
$GaCl_3$	H_2O	5 7	-58	PMR (a)	78
Mg^{2+}					
$Mg(ClO_4)_2$	H_2O	5 8±0 2	-72– -82	PMR (a)	72,78
$Mg(ClO_4)_2$	H_2O	6±0 3	-67– -90	PMR (a)	25
	CH_3OH	6 0±0 07	-25– -80	PMR (a)	25
		6	-67.5– -80	PMR (a)	80
	C_2H_5OH	5 9±0 4	-60– -90	PMR (a)	82
	NH_3	5 9±0 1	-75	PMR (a)	77*b*
$Mg(NO_3)_2$	H_2O	6±0 3	-67– -90	PMR (a)	25
$Mg(BF_4)_2$	NH_3	5 9±0 1	-75	PMR (a)	77*b*
Cr^{3+}					
$Cr(ClO_4)_3$	H_2O	6 2±0 2	25	^{18}O ID	19
		6	ca 20	^{17}O NMR (a)	131
	dmso	6	60	Ion ex	28
	pyridine-*N*-oxide	6	70	Ion ex	33
	CH_3OH	6	60	Ion ex	29
$Cr(NO_3)_3$	NH_3	6.0±0 2	-50	^{15}N ID	22
Ni^{2+}					
$Ni(ClO_4)_2$	H_2O	4 or 6	36	^{17}O NMR (a)	132
	CH_3OH	4 8±0 7	-10	PMR (a)	133
$Ni(NO_3)_2$	H_2O	6 0±0 2	-30	PMR (a)	84
[g]Ni^{2+}	dmso	5 9±0 2	h	PMR (a)	128
Miscellaneous					
$Sc(NO_3)_3$	H_2O	5 1	h	PMR (a)	75
$Th(ClO_4)_4$	H_2O	9 1	-100	PMR (a)	75
[g]Sn^{4+}	H_2O	6	h	PMR (a)	75
[g]UO_2^{2+}	H_2O	4	h	PMR (a)	75
[g]Zn^{2+}	H_2O	6	h	PMR (a)	75
KOH	H_2O	4	h	X-ray	15, 16
$Rh(ClO_4)_3$	H_2O	5 9±0 4	64.4–79	^{18}O ID	21
$In(ClO_4)_3$	H_2O	5 8±6 0	-89– -99	PMR (a)	78
[i]$Co(NO_3)_3$	NH_3	6 0±0 2	-78	PMR (a)	77*a*
$Zn(ClO_4)_2$	CH_3OH	6	-82	PMR (a)	83
$Zn(NO_3)_2$	CH_3OH	6	-82	PMR (a)	115
$(CH_3)_3Pt(ClO_4)$	H_2O	3 0±0 1 2 9±0 1	5	^{17}O NMR (a)	88, 89
$(NH_3)_2Pt(ClO_4)_2$	H_2O	1 8±1 3	29	^{17}O NMR (s)	89
		1 6±0 3	60	^{17}O NMR (a)	89
		1.9±0 1	60	^{17}O NMR (a)	89
	CH_3CN	2.0±0.1	-81	PMR (a)	90

Notes to Table I

[a] Cation. in those cases where several determinations are reported the table is headed M^{n+} and the metal salt used is then given. In the section headed "miscellaneous" only the metal salt is indicated. [b] Solvent the solvent to which CN refers is indicated in this column In some cases the bulk solvent may have contained an inert diluent. [c] CN the reported CN values are fully listed except where the author has given raw experimental data over a range of conditions – in these cases the extreme range of the data is listed. Error estimates are only shown when given in the original work. [d] Temperature (°C)· the temperature range over which CN values were determined is shown. [e] Method· ^{15}N ID, ^{15}N isotope dilution, ^{18}O ID, ^{18}O isotope dilution, ion ex , ion exchange and chemical analysis; PMR, proton magnetic resonance, ^{17}O NMR, ^{17}O nuclear magnetic resonance, ^{14}NMR, ^{14}N nuclear magnetic resonance, (a) or (s) after the method indicates area method or shift method respectively [g] Salt not specified [h] Temperature not specified. [i] Dissolved as $[Co(NH_3)_6](NO_3)_3$ [f] Several diluent solvents employed – nearest integer listed for CN

value exhibited by Al^{3+} in that solvent Such an argument seems applicable to other metal ion solutions also.

In several cases CN is found to be identical to the cation solvation number in the solid water state, e.g. $Cr(H_2O)_6{}^{3+}$ (Ref. 19), $Ni(H_2O)_6{}^{2+}$ (Ref. 84), $Co(CH_3CN)_6{}^{2+}$ (Ref. 85) and $Co(dmf)_6{}^{2+}$ (Ref. 86) For $Co(H_2O)_6{}^{2+}$ cobalt–oxygen bond distances are found to be similar in solution and the solid state[11,12]. Despite the above comparisons it would seem to be inadvisable to draw rigid analogies between solid-state solvation numbers and CN values especially for ions which exhibit variable solid-state solvation numbers such as the Ni^{2+}–acetonitrile system[87] in which the distinct species $[Ni(CH_3CN)_6](ClO_4)_2$, $[Ni(CH_3CN)_4(ClO_4)_2]$ and $[Ni(CH_3CN)_2(ClO_4)_2]$ have been identified in the solid state

The last three entries in Table I are examples of the complete characterisation of the first coordination sphere of Pt complexes in solution. The solid state stoichiometry of the Pt^{4+} species is $(CH_3)_3PtClO_4$ (Ref. 88, 89) whereas in solution it is $[(CH_3)_3Pt(H_2O)_3]ClO_4$ and exists as the fac octahedral species. Similarly in water[89] and acetonitrile[90] $(NH_3)_2Pt(ClO_4)_2$ coordinates two solvent molecules to produce the square planar species $[(NH_3)_2Pt(solvent)_2]^{2+}$

D. MIXED SOLVATION IN THE FIRST COORDINATION SPHERE

The title of this section suggests the possibility of two convergent view points from which solutions of metal ions in mixed solvents may be considered. Thus the familiar transition metal ion systems in aqueous ammonia or aqueous 1,2-diaminoethane are often cited as classic examples of complex formation[91,92] equilibria, and yet may equally well be considered as examples of mixed solvation Clearly terminology in this area is a matter of semantics The discussion to follow is restricted largely to data obtained via the direct PMR and ion exchange techniques described in section B, by virtue of the bias of reported studies in this area

King et al. have reported mixed solvation studies of Cr^{3+} in two-component aqueous solvent systems in which the second component has been either methanol[29–31], ethanol [29–32], pyridine-*N*-oxide [33] or dmso[28] The observed solvent equilibria may be written:

$$\mathrm{Cr(OH_2)_{7-n}(solvent)_{n-1}^{3+} + solvent \rightleftharpoons Cr(OH_2)_{6-n}(solvent)_n^{3+} + H_2O}$$

where "solvent" is not water. A cation exchange resin technique was employed to isolate species in which n varied from 0 to 6 for those systems in which the second solvent was either methanol, pyridine-N-oxide, or dmso (Fig 4) and in the case of the last two solvents isomeric species were isolated when $n = 2$, 3 and 4 In the water–ethanol system species in which $n = 0$ to 4 were separated, but no isomers were observed The relative tendency for binding of water and either methanol, ethanol, or dmso to Cr^{3+} depends upon the composition of the first coordination sphere. Whilst Q_n, where

$$Q_n = \frac{[\mathrm{Cr(OH_2)_{6-n}(solvent)_n^{3+}}]\, a_{\mathrm{H_2O}}}{[\mathrm{Cr(OH_2)_{7-n}(solvent)_{n-1}^{3+}}]\, a_{\mathrm{solvent}}}$$

decreases as n increases for methanol, ethanol, and dmso over the respective ranges $Q_1 = 0.65 - Q_6 = 0.0022$ (60°C), $Q_1 = 0.42 - Q_4 = 0.0134$ (75°C), and $Q_1 = 220 - Q_6 \approx 15$ (60°C); correction of these values for statistical effects[93,94] indicated that whereas the tendency for methanol and ethanol to enter the first coordination sphere decreased with increase in n the opposite trend was the case for dmso The tendency for pyridine-N-oxide to enter the first coordination sphere does not vary appreciably with changes in n. The trends in Q_n for the water–alcohol systems were rationalised via a model in which steric interactions localised along the twelve edges of an octahedron defined by the six-coordinated solvent molecules were the predominant factor in determining the relative stabilities of the various Cr^{3+} complexes. Steric factors were considered to be less important in the dmso and pyridine-N-oxide systems Other workers[95] have also studied the

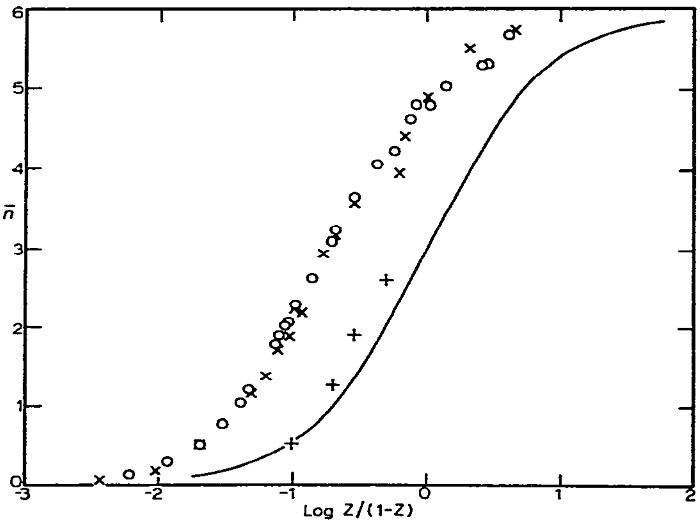

Fig 4 The average number of dmso molecules, $\bar{n}$, in the first coordination sphere of Cr^{3+}, (o, ×) and Al^{3+} (+), as a function of dmso mole fraction Z The solid line gives $\bar{n}$ values expected on the basis of random solvation i e $\bar{n}/(6-\bar{n}) = Z/(1-Z)$ (after Fig 1, Ref 28).

solvation of Cr^3 in aqueous dmso and reach similar conclusions to those above, but there is a suggestion[28] that in this case non-equilibrium conditions may have pertained. Proton magnetic resonance peak area studies of the solvation of Al^3 in aqueous dmso[39] show this ion to be preferentially solvated by water at water mole fractions $\geqslant$ 0 80 and by dmso at water mole fraction $\leqslant$ 0 75. A total CN of 6 was observed over the water· dmso mole fraction ratio range 1·56–8:38 It has also been observed that Al^{3+} discriminates less in favour of water over dmso than does Cr^{3+} (see Fig. 4).

From a number of mixed solvation studies of Al^{3+} two broad categories of solvent emerge[38,39,96]:

(*1*) solvents which compete with water for coordination sites, e g dmf, dmso, acetonitrile, tetramethylenesulphoxide,

(*2*) solvents which do not compete with water for coordination sites, e g acetone, tetrahydrofuran, dimethyl sulphate, dimethyl sulphone, tetramethylene sulphone, tetramethylurea, dioxane In the cases of the above sulphoxide, sulphone and sulphate solvents it is reported[38] that solvating ability is mainly dependent upon basicity such that only the more basic solvents dmso and tetramethylene sulphoxide compete effectively with water In addition there appears to be a steric restriction on solvation by tetramethylene sulphoxide. Solvating ability does not appear to depend upon the solvent molecular dipole moment Acetone (μ = 2.7 D), tetramethylurea (μ = 3 3 D), dmf (μ = 3 9 D), and dmso (μ = 3.9 D) are all highly polar, yet only the latter two can compete with water for occupancy of the first coordination sphere of Al^{3+} Reduction of the $H_2O.Al^{3+}$ mole fraction to less than 6 enables both acetone and tetrahydrofuran[38] to coordinate to Al^{3+}. Under similar conditions acetone also coordinates to Ga^{3+} (Refs. 97,98)

Both dmso and dmf compete with water for coordination sites on Ni^{2+} and Co^{2+}, but dioxane does not[99]. In aqueous methanol solvent both $[Co(methanol)_5(H_2O)]^{2+}$ and $[Co(methanol)_4(H_2O)_2]^{2+}$ have been identified in solution[100], but the identification of isomers of the latter species has been subject to discussion[53] Studies of Mg^{2+} in aqueous methanol indicate that both solvents coordinate simultaneously[101] but acetone competes with neither solvent[25].

Of the systems so far reported there appears to be no case of apparent total CN variation as solvent composition has been varied, which cannot be explained via the entry of an anion into the first coordination sphere, as is discussed in section E.

E. CONTACT ION PAIRS

The detection of contact ion pairs, or inner sphere complexes, formed by the replacement of solvent in the first coordination sphere by anions has to some extent been a by-product of CN studies.

In aqueous solution perchlorate ion has a relatively low coordinating ability and CN investigations of aqueous perchlorate solutions of the ions[102] Al^{3+}, Be^{2+}, Co^{2+}, Cr^{3+}, Ga^{3+}, In^{3+} and Th^{4+} show little evidence for contact ion pair formation In concentrated perchloric acid, however, time-dependent changes of $Cr(ClO_4)_3$ solutions[103], and the broadening of the ^{35}Cl NMR resonance in $Mn(ClO_4)_2$ solutions[104] have been interpreted in terms of perchlorate contact ion pair formation It has been suggested that the lower water activity encountered in these latter studies may be an important factor in the formation of the postulated contact ion pairs

Where other salts have been used in CN determinations in aqueous solution, contact ion pairs have assumed a greater importance. Thus aqueous $AlCl_3$ (2.70 *M*) and $GaCl_3$ (2.42 *M*) solutions show little sign of contact ion pairing, but both *cis*- and *trans*-$Be(H_2O)_4Cl_2$ have been suggested as possible explanations of the complexities of the PMR signals arising from coordinated water in 0.25 *M* $BeCl_2$ solution[78].

A recent study[105] of the aqueous aluminium(III) fluoride system via ^1H, ^{19}F and ^{21}Al NMR detected four contact ion pairs as shown in the scheme.

$$2\,AlF(H_2O)_5{}^{2+} \rightleftharpoons Al(H_2O)_6{}^{3+} + AlF_2(H_2O)_4{}^{+} \qquad Q_1 = 0\ 15 \tag{1}$$

$$AlF_2(H_2O)_4{}^{2+} \rightleftharpoons AlF_3(H_2O)_3 + AlF_2(H_2O)_4{}^{+} \qquad Q_2 = 0.14 \tag{2}$$

$$AlF_3(H_2O)_3 \rightleftharpoons AlF_4(H_2O)_2{}^{-} + AlF_2(H_2O)_4{}^{+} \qquad Q_3 = 0.038 \tag{3}$$

where Q_n is the equilibrium quotient at −15°C. Separate ^{19}F resonances were observed for each of the fluoro contact ion pairs, but the proton chemical shifts for coordinated water in each such species were so similar that only a single proton resonance attributed to coordinated water was observed Nevertheless area measurements were consistent with the hexacoordinated species formulated in Eqns (1)–(3) In a similar manner ^9Be and ^{19}F NMR have been employed to detect $BeF_4{}^{2-}$, $BeF_3{}^{-}$ in aqueous solution[106], but coordinated water was not detected via PMR and hence the first coordination sphere was not completely characterised

The addition of acetone to aqueous gallium halide solutions causes a considerable decrease from 6 in the value of CN for water as deduced from PMR area measurements The observation of two ^{69}Ga NMR resonances in these solutions led to the postulation of $Ga(H_2O)_6{}^{3+}$ and $GaX_4{}^{-}$ as major species where X = Cl, Br or I The major effect of acetone is to lower the dielectric constant The species $GaCl_4{}^{-}$ has also been shown to exist in concentrated hydrochloric acid media[107] via ^{71}Ga NMR.

In aqueous nitrate solutions CN values of 5 1 and 2 9 for Sc^{3+} and Th^{4+}, respectively, have been interpreted in terms of nitrate contact ion pairs[75]. The latter value should be contrasted with 9.1 observed in aqueous perchlorate solutions of Th^{4+} By contrast the CN value for Al^{3+} in aqueous nitrate solution[35] is 6.01 indicating virtually no contact ion pairing This is a particularly interesting result, as IR and Raman data show the nitrate site symmetry to be lowered from D_{3h} to C_{2v} in aqueous $Al(NO_3)_3$ solutions[108]. Evidently the pertinent interaction occurs within a solvent separated ion pair[35,109]. This is consistent with the suggested[110] high ordering in the second coordination sphere of Al^{3+}.

In solvents with dielectric constants lower than that of water the formation of contact ion pairs is more prevalent. The $AlCl_3$–acetonitrile[111,112] system provides a good example of this Two PMR studies have given CN values close to 1.5 for acetonitrile in $AlCl_3$ solutions of close to 3 *M* concentration An ^{27}Al NMR study[112] showed that these solutions exhibited two resonances of relative area 3 1 and hence the following scheme for the dissolution of $AlCl_3$ in acetonitrile was proposed.

$$4\,AlCl_3 + 6\,CH_3CN \rightleftharpoons 3\,AlCl_4{}^{-} + Al(CH_3CN)_6{}^{3+}$$

This is consistent with the observation of Raman lines due[113] to $AlCl_4{}^{-}$. Similarly CN values of 2.8 and 2.9 for $Al(ClO_4)_3$ in acetonitrile suggest entry of $ClO_4{}^{-}$ into the first coordination sphere, and it appears from the complexity of the PMR spectra of the coordi-

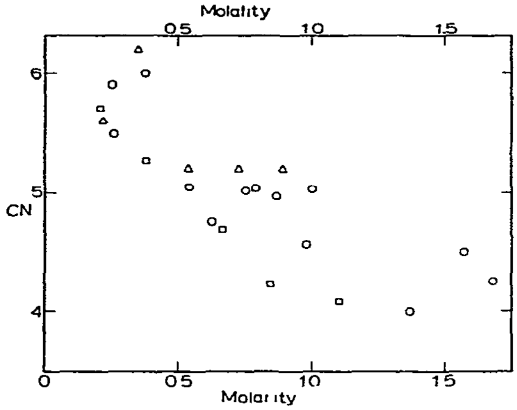

Fig 5. The variation of CN for Zn^{2+} with salt concentration is methanol solvent Circles and squares are data points for $Zn(ClO_4)_2$ and $Zn(NO_3)_2$, respectively in molar concentration units at −82°C Triangles are data points for $Zn(ClO_4)_2$ in molal concentration units at −81°C Data from Refs 83, 115 and 114, respectively.

nated acetonitrile that several solvent containing species may exist in the system[96,111] In the $Zn(ClO_4)_2$–methanol system the observed Cn decreased from 6 to 4 as the $Zn(ClO_4)_2$ concentration was increased to 1.8 *M* (Fig 5) On this basis the species $Zn(CH_3OH)_4(ClO_4)_2$ and $Zn(CH_3OH)_5ClO_4^+$ were postulated[83] A similar rationale[80] was applied to the observation of a CN value of 5.7 ± 0.1 for Mg^{2+} in methanolic solution of $Mg(ClO_4)_2$. Similarly[114] the observation of a solution number significantly less than 6 for Zn^{2+} and Mg^{2+} in methanolic solutions of their perchlorate salts might be explained via contact ion pairs

An alternative explanation[115], to that of the formation of contact ion pairs, has recently been advanced by Al-Baldawi et al in a recent PMR area study to rationalise the apparent decrease in CN of Zn^{2+} in methanol from ca. 6 to 4 (Fig. 5) as the concentration of Zn^{2+} (nitrate) was increased. IR and Raman measurements suggested that no $Zn^{2+}NO_3^-$ contact ion pairs exist at the temperature at which the PMR study was carried out (−82°C) and the following rationalisation of the apparent decrease in CN was suggested. In the event that methanol occupies three different sites (*1*) bound between Zn^{2+} and NO_3^- in a solvent separated ion pair, (*2*) bound in the remaining sites in the first coordination sphere of Zn^{2-}, and (*3*) bulk methanol, then when environmental averaging between (*1*) and (*2*) and between (*2*) and (*3*) is slow, but is fast between (*1*) and (*3*), resonance (*1*) will not appear in the resonance attributed to the coordinated solvent and consequently the observed CN will be less than the true value. This argument requires that the anion of the solvent separated ion pair should cause rapid solvent exchange between bulk solvent and that portion of the first coordination sphere adjacent to the anion. The kinetic studies most relevant to this argument would appear to be those involving the exchange of dmf solvent on $Al(dmf)_6{}^{3+}$ where the rate constants for the chloride, bromide, iodide[116] and perchlorate[117] salts were 11 0, 0 36, 0 38 and 0 20 sec^{-1} at 25°C Chloride ion accelerates the dmf exchange rate by a factor of ca. 30 by comparison with bromide and iodide, but in each case CN was observed to be 5.7 ± 0 3 (0 20–0 26 *M* solutions – PMR area method) despite the differences in solvent exchange rate, which may presumably be interpreted in terms of variation of the characteristics of solvent ion pairs Further investigations of correlations between solvent exchange rate, CN and total salt concentration would be of considerable interest in view of the proposals of Al-Baldawi et al

Ion pairing has been discussed in this section only where it impinges upon CN studies For more general information in this area the reader is directed to recent reviews[118–120]

F CONCLUSION

The experimental distinguishability of solvent molecules in the first coordination sphere of metal ions from those in the bulk solvent is amply illustrated by the CN studies considered in this review The extension of these studies over a greater range of solvents and metal ions appears to be inevitable Isotopic dilution and ion exchange methods are limited in applicability to the more inert systems, but the various NMR methods will doubtless be employed over a greater range of systems and should be enhanced by the greater magnetic fields, and wider operating temperature ranges now commercially available. Nevertheless solvent exchange processes in some of the more labile systems are too rapid to permit direct CN studies via NMR, and it is in this area that the solution X-ray methods are likely to prove of great use

The intrinsic interest of CN data apart, there are two areas of coordination chemistry to which CN studies are of particular relevance The first such area is that of metal ion substitution reactions in solution, in which mechanistic rationales[5,121,122] are frequently based upon comparison of ligand substitution and solvent exchange rates In the majority of cases where *direct* determinations of the rate of solvent exchange on metal ions in solution have been made, NMR line-broadening methods have been used[4,73] These methods measure τ_m, the life time of a particular solvent molecule in the first coordination sphere, which is equal to the reciprocal of k_m, the specific first-order rate constant for exchange of a particular solvent molecule ($\tau_m = k_m{}^{-1}$) Thus the total solvent exchange rate, R, of the metal ion is given by[123]

$$R = k_m(\mathrm{CN})\ [\text{metal ion}]$$

The metal ion CN value is clearly central to the calculation of R, and hence to mechanistic arguments in which R assumes importance.

The second area is that of non-transition metal ion complex formation in solution, a field which has not advanced as rapidly as the analogous area of transition metal chemistry, due largely to the lack of d–d electronic transitions and hence the restricted applicability of spectrophotometric techniques. The complete and quantitative determination of the composition of the first coordination sphere with respect to both solvent and other ligands by NMR methods, as exemplified by investigation of the Be^{2+}, Al^{3+} and Ga^{3+}, 2,4-pentadionato system[40,41] and the aluminium(III) fluoride system[105] clearly points the way for further work in this area

REFERENCES

1 F J Garrick, *Phil Mag*, 9 (1930) 131
2 F J. Garrick, *Phil Mag*, 10 (1930) 76
3 J.D. Bernal and R H Fowler, *J Chem Phys*, 1 (1933) 515.
4 G H Langford and T R Stengle, *Coord Chem Rev*, 2 (1967) 349
5 M Eigen and R G Wilkins *Mechanisms of Inorganic Reactions, Advan Chem Ser., No 49*, American Chemical Society, Washington D C, 1965
6 D J. Hewkin and R H Prince, *Coord Chem Rev*, 5 (1970) 45
7 R.F Kruh, *Chem Rev*, 62 (1962) 319
8 H A Levy and M D Danford, *J Amer Chem Soc*, 84 (1962) 3965
9 D L Wertz and R F Kruh, *J Chem Phys*, 47 (1967) 388
10 H Taube, *Progr Stereochem*, 3 (1962) 95.
11 D L Wertz and R F Kruh, *J Chem Phys*, 50 (1969) 4313
12 D L Wertz and R F Kruh, *Inorg Chem*, 9 (1970) 595.
13 A F Kapustinokii and V A Solokhin, *Khim Tekhnol*, 4 (1958) 3
14 R C Schoonmaker, A H Friedmann and R F Porter, *J Chem Phys*, 31 (1959) 1586
15 G W. Brady and J T Krause, *J Chem Phys*, 27 (1957) 304
16 G W Brady *J Chem Phys*, 28 (1958) 464
17 G W. Brady, *J Chem Phys*, 33 (1960) 1079
18 G W. Brady, *J Chem Phys* 29 (1958) 1371
19 J P. Hunt and H Taube, *J Chem Phys* 18 (1950) 757
20 H.W Baldwin and H Taube, *J Chem Phys*, 33 (1960) 206
21 W Plumb and G M Harris, *Inorg. Chem* 3 (1964) 542
22 H H Glaeser and J P Hunt, *Inorg Chem*, 2 (1964) 1246
23 T E. Rogers, J H. Swineheart and H Taube, *J Phys Chem*, 69 (1965) 134
24 J H Swinehart, T E Rogers and H Taube, *J Chem Phys*, 38 (1963) 398
25 N A Matwiyoff and H Taube, *J Amer. Chem Soc* 90 (1968) 2796
26 A C Rutenberg and H Taube, *J Chem Phys* 20 (1952) 825
27 F A Posey and H. Taube, *J Amer Chem Soc*, 75 (1953) 4099
28 L P Scott, T.J. Weeks, D E Bracken and E.L. King, *J Amer Chem. Soc* 91 (1969) 5219
29 C.C Mills and E L. King, *J Amer Chem Soc*, 92 (1970) 3017
30 J C. Jayne and E.L. King, *J Amer Chem Soc*, 86 (1964) 3989.
31 R.J. Baltisberger and E L. King, *J. Amer Chem Soc*, 86 (1964) 795
32 D W Kemp and E.L. King, *J Amer Chem Soc*, 89 (1967) 3433
33 T.J. Weeks and E L. King, *J. Amer. Chem. Soc* 90 (1968) 2545
34 J A Pople, W.G Schneider and H J Bernstein *High Resolution Nuclear Magnetic Resonance*, McGraw–Hill, New York, 1959, p. 223.
35 N A Matwiyoff, P E. Darley and W.G. Movius, *Inorg Chem*, 7 (1968) 2173.
36 A. Fratiello, R.E. Lee, V.M Nishilda and R E Schuster, *Chem Commun*, (1968) 173
37 A. Fratiello, R.E Lee, V M Nishilda and R E Schuster, *J. Chem. Phys*, 47 (1967) 4951
38 A Fratiello, R E Lee, V M Nishilda and R E. Schuster, *Inorg. Chem.*, 8 (1969) 69.
39 S Thomas and W L Reynolds, *Inorg. Chem*, 9 (1970) 78
40 N A. Matwiyoff and W G. Movius, *J Amer Chem Soc*, 89 (1967) 6077
41 W.G. Movius and N A Matwiyoff, *J Amer Chem Soc*, 90 (1968) 5452.
42 W G. Movius and N A Matwiyoff, *Inorg Chem* 8 (1969) 925.
43 D.A Buckingham, I. Durham and A M Sargeson, *Australian J. Chem*, 20 (1967) 257
44 L.G. Warner, N.J. Rose and D.H. Busch, *J. Amer. Chem. Soc*, 89 (1967) 703.

45 J A Jackson, J F. Lemons and H Taube, *J Chem Phys*, 32 (1960) 553
46 R E Connick and D N Fiat, *J. Chem Phys*, 39 (1963) 1349
47 D. Fiat and R.E. Connick, *J. Amer. Chem. Soc.*, 88 (1966) 4754
48 H H Glaeser, H.W. Dodgen and J.P Hunt, *J Amer Chem Soc*, 89 (1967) 3065.
49 M. Alei and J A. Jackson, *J. Chem Phys*, 41 (1964) 3402.
50 J Reuben and D Fiat, *Inorg Chem*, 6 (1967) 579
51 Z Luz and R G Schulman, *J Chem Phys*, 43 (1965) 3750
52 C.C. McDonald and W.D. Phillips, *J Amer Chem Soc*, 85 (1963) 3736
53 W D Horrocks and J R. Hutchison, *J Chem Phys*, 46 (1967) 1703
54 J.O. Bockris, in *Modern Aspects of Electrochemistry*, J O Bockris and B.E Conway (Eds), Butterworths, London, 1954, p 63
55 S. Broersma, *J Chem. Phys*, 28 (1958) 1158
56 J.F. Hinton and E S. Amis, *Chem. Rev*, 67 (1967) 367.
57 W J. Hamer, *The Structure of Electrolyte Solutions*, Wiley, New York, 1959
58 R A. Robinson and R H Stokes, *Electrolyte Solutions*, Butterworths, London, 1959
59 D S McClure, *J Phys Chem Solids*, 3 (1957) 311
60 J D. Dunitz and L E. Orgel, *J Phys Chem Solids*, 3 (1957) 20, 318
61 O Schmitz-Dumont, H Gossling and H Brokopf, *Z. Anorg Chem*, 300 (1959) 157
62 O G. Holmes and D S McClure, *J Chem Phys*, 26 (1957) 1686
63 O Schmitz-Dumont, H Brokopf and K Burkhardt, *Z Anorg Chem*, 295 (1958) 7
64 F E Ilse and H. Hartmann, *Z Phys Chem*, 197 (1951) 239
65 F E Ilse and H Hartmann, *Z Naturforsch*, 6A (1951) 751.
66 H Hartmann and H L. Schlafer, *Z Naturforsch.*, 6A (1951) 754, 760.
67 H.L Schlafer, *Z. Phys Chem (N F)* 4 (1955) 116
68 L E Orgel, *J Chem Phys*, 23 (1955) 1824
69 C.K. Jørgensen, *Acta Chem Scand.* 8 (1954) 1495
70 C K Jørgensen, *Acta Chem Scand*, 9 (1955) 717
71 C K Jørgensen, *Acta Chem Scand*, 11 (1957) 73
72 C K Jørgensen, *Acta Chem. Scand* 11 (1957) 399
73 T J Swift and R E Connick, *J Chem Phys.*, 37 (1962) 307.
74 T J Swift, *Inorg Chem*, 3 (1964) 526
75 A Fratiello, R E Lee and R E Schuster, *Inorg Chem*, 9 (1970) 391
76 N A. Matwiyoff and P E Darley, *J Phys Chem* 72 (1968) 2659
77 (*a*) T J. Swift and H H Lo, *J Amer Chem Soc*, 89 (1967) 3988, (*b*) L W Harrison and T J Swift, *J. Amer Chem Soc*, 92 (1970) 1963
78 A Fratiello, R E Lee, V M Nishida and R E Schuster, *J. Chem Phys*, 48 (1968) 3705
79 A Fratiello, R E Lee, V M Nishida and R E Schuster, *Chem Commun.*, (1968) 173.
80 S Nakamura and S. Meiboom, *J Amer Chem Soc*, 89 (1967) 1765
81 J H Swinehart and H Taube, *J. Chem Phys*, 37 (1962) 1579
82 T.D Alger, *J Amer Chem Soc*, 91 (1969) 2220
83 S A Al-Baldawi and T.E Gough, *Can J Chem*, 47 (1969) 1417
84 T J Swift and G P Weinberger, *J Amer Chem Soc*, 90 (1968) 2023
85 N.A. Matwiyoff and S.V Hooker, *Inorg Chem.*, 6 (1967) 1127
86 N A Matwiyoff, *Inorg Chem*, 5 (1966) 788
87 A.E Wickenden and R A. Krause, *Inorg Chem*, 4 (1965) 404
88 G E. Glass and R S Tobias, *J Amer. Chem. Soc*, 89 (1967) 6371
89 G E. Glass, W B Schwabacher and R S Tobias, *Inorg Chem*, 7 (1968) 2471
90 J F O'Brien, G.E Glass and W L Reynolds, *Inorg Chem*, 7 (1968) 1664
91 J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*, Haase, Copenhagen, 1941
92 F.J C. Rossotti, in. *Modern Coordination Chemistry*, J Lewis and R.G Wilkins (Eds), Interscience, New York, 1960, Chap. 1
93 S W. Benson, *J Amer Chem Soc*, 80 (1958) 5151.
94 E L King, *J Chem Educ*, 43 (1966) 478.

95 K.R Ashley, R E Hamm and R.H Magnuson, *Inorg Chem* , 6 (1967) 413.
96 L D Supran and N. Sheppard, *Chem. Commun,* (1967) 832
97 A. Fratiello, R.E. Lee and R.E Schuster, *Inorg Chem.*, 9 (1970) 82
98 A. Fratiello, R E. Lee and R E Schuster, *Chem. Commun.*, (1969) 37.
99 L S. Frankel, T R. Stengle and C H Langford, *Can J. Chem* , 46 (1968) 3183
100 Z Luz and S Meiboom, *J Chem Phys* , 40 (1964) 1058
101 J.H. Swinehart and H Taube, *J Chem Phys* , 37 (1962) 1579
102 See Table 1 (pp. 319, 320) for Refs.
103 K M Jones and J. Bjerrum, *Acta Chem. Scand* , 19 (1965) 974.
104 F Klanberg, J P. Hunt and H W Dodgen, *Inorg Chem* , 2 (1963) 139
105 N A. Matwiyoff and W.E. Wageman, *Inorg Chem* , 9 (1970) 1031
106 J C. Kotz, R. Schaeffer and A. Close, *Inorg Chem* , 6 (1967) 620
107 J.W Akitt, N N Greenwood and A. Storr, *J. Chem Soc* , (1965) 4410
108 R E. Hester and R A Plane, *J. Chem Phys* , 40 (1964) 411.
109 R E. Irish, G. Chang and D L Nelson, *Inorg. Chem* , 9 (1970) 425.
110 E R. Malinowski and P.S Knapp, *Inorg Chem* 48 (1968) 4989
111 J F. O'Brien and M. Alei, *J Phys Chem* , 72 (1970) 743.
112 J F Hon, *Mol Phys* , 15 (1968) 57
113 C D Schmulbach, *J Inorg Nucl Chem* , 26 (1964) 745.
114 R N Butler and M C R Symons, *Trans Faraday Soc* , 65 (1969) 945
115 S A. Al-Baldawi, M.H Brooker, T.E. Gough and D.E Irish, *Can J. Chem* , 48 (1970) 1202
116 A Fratiello and R E Schuster, *J Phys Chem* , 71 (1967) 1948
117 W G Movius and N A Matwiyoff, *Inorg Chem* , 6 (1967) 347
118 V. Gutmann, *Coordination Chemistry in Non-Aqueous Solutions,* Springer Verlag, Vienna, 1968
119 M.T Beck, *Coord Chem Rev* , 3 (1968) 91
120 L G. Sillen and A E Martell, *Stability Constants of Metal-Ion Complexes,* The Chemical Society, London, 1964
121 C H Langford and T R Stengle, *Ann Rev Phys Chem* , 19 (1968) 193
122 D J Hewkin and R H Prince, *Coord Chem Rev* , 5 (1970) 45
123 H H. Glaeser, H W Dodgen and J P Hunt, *Inorg Chem* , 4 (1965) 1061
124 W.G Movius and N A Matwiyoff, *J Phys Chem* , 72 (1968) 3063
125 A Takahashi, *J Phys Soc Japan,* 24 (1968) 657
126 A Fratiello and R E. Schuster, *J Phys Soc Japan,* 47 (1967) 1554
127 S Thomas and W L Reynolds, *J Chem Phys* , 44 (1966) 3148
128 L S Frankel, *Chem Commun.*, (1969) 1254.
129 D Fiat and R E Connick, *J Amer Chem Soc* , 88 (1966) 4754.
130 T.J. Swift, O.G. Fritz and T A Stephenson, *J Chem Phys* , 46 (1967) 406
131 M Alei, *Inorg Chem* , 3 (1964) 44
132 R E. Connick and D Fiat, *J Chem Phys* , 44 (1966) 4103
133 Z Luz and S Meiboom, *J Chem Phys* , 40 (1964) 1066

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