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COORDINATION CHEMISTRY OF CERTAIN TRANSITION-METAL IONS. THE ROLE OF THE SOLVENT

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ABBREVIATIONS

acac	acetylacetonate
AN	acetonitrile
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
PDC	propanediol-1,2-carbonate
TMP	trimethyl phosphate

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A. INTRODUCTION

Coordination chemistry is making increasing use of non-aqueous solvents as reaction media. Most of the usual solvents are donor solvents and thus play a considerable rôle in coordination chemistry in solution. When an acceptor compound A is dissolved and solvated the interaction with the solvent D will be a donor–acceptor reaction

$$A + nD \rightleftharpoons AD_n$$

A "complex reaction" is then a replacement or ligand-exchange reaction in which solvent molecule(s) are replaced by competitive ligand(s) X which should have stronger coordinating properties than the solvent molecules:

$$AD_n + mX \rightleftharpoons AX_m + nD$$

In order to choose a suitable solvent for a particular reaction, the donor properties of the solvents should be known. It is understood that different solvents have different coordinating properties, but no measurable quantity representing the degrees of donor properties has been available until recently.

B. THE DONOR NUMBER

The interaction of a covalent acceptor molecule, such as $SbCl_5$, capable of increasing its coordination number by one unit with different O-donor solvent molecules, D, has been measured calorimetrically in an inert medium[1]

$$SbCl_{5(\text{dissolved})} + D_{(\text{dissolved})} \rightleftharpoons D \cdot SbCl_{5(\text{dissolved})}; \quad -\Delta H_{D \cdot SbCl_5}$$

The figures obtained were found to be proportional to the thermodynamic equilibrium constants K obtained from spectrophotometric[1,2], and n.m.r. measurements[3]

TABLE 1

$-\Delta H_{D\cdot SbCl_5}$ AND LOG $K_{D\cdot SCbl_5}$-VALUES FOR SEVERAL DONOR SOLVENTS (D)

Donor	$-\Delta H$ *(kcal/mol)*	*log* $K_{D\cdot SbCl_5}$
$SOCl_2$	0.4	0.3
$POCl_3$	11.7	0.7
CH_3CN	14.1	2.8
PDC	15.1	3.0
Acetone	17	4.87
H_2O	18	5.3
Ether	19.2	5.5
TMP	23	9.3
Tributylphosphate	24	10.5
DMSO	29.8	11

(Table 1), showing that the entropy contributions are equal for the solvent–acceptor interactions under consideration.

It would be desirable to calculate $-\Delta H$-values for other donor–acceptor reactions. An empirical approach is allowed for certain systems, since the $-\Delta H_{\mathrm{D\cdot SbCl_5}}$-values were found nearly proportional to the $-\Delta H_{\mathrm{D\cdot A}}$-values obtained when A is $SbCl_3$[4], $SbBr_3$[4], $(CH_3)_3SnCl$[5], I_2 or C_6H_5OH[1] (Table II). This would indicate that there are no considerable contributions due to specific interactions between the solvent molecules and the acceptor molecules under consideration.

TABLE 2

$-\Delta H_{\mathrm{A\cdot D}}$-VALUES FOR REACTIONS OF DONOR SOLVENTS WITH DIFFERENT ACCEPTOR MOLECULES IN "INERT" MEDIA

Donor	*Acceptor*					
	$SbCl_5$	*$SbCl_3$*	*$SbBr_3$*	*C_6H_5OH*	*I_2*	*$(CH_3)_3SnCl$*
$POCl_3$	11.7	—	—	2.5	—	—
CH_3CN	14.1	—	—	3.2	1.9	4.8
CH_3COOCH_3	16.4	—	—	3.2	2.5	—
$(CH_3)_2CO$	17.0	—	—	3.3	2.5	5.7
$CH_3COOC_2H_5$	17.1	—	—	4.8	—	—
$C_6H_5POCl_2$	18.5	4.4	3.7	3.4	—	—
$(C_2H_5)_2O$	19.2	—	—	5.0	4.3	—
$(CH_3O)_3PO$	23.0	6.1	5.2	5.3	—	—
$HCON(CH_3)_2$	26.6	7.4	6.8	6.1	3.7	—
$CH_3CON(CH_3)_2$	27.8	—	—	6.4	4.0	7.9
$(CH_3)_2SO$	29.8	8.8	8.3	6.5	4.4	8.2
C_5H_5N	33.1	9.9	—	8.1	7.8	(6.5)

If such a linear relationship holds for other acceptors, the measurement of $-\Delta H$-values for 2 donor molecules should allow us to obtain approximate values of $-\Delta H$ for interactions with numerous other donor molecules.

This leads to the suggestion that the donor number *DN* of a solvent may be defined as the numerical $-\Delta H_{\mathrm{D\cdot SbCl_5}}$-value for the respective solvent[6–8]:

$$DN_{\mathrm{SbCl_5}} \equiv -\Delta H_{\mathrm{D\cdot SbCl_5}}$$

The donor number is nearly a molecular property of the solvent molecules and expresses the total amount of interaction with an acceptor molecule including the contributions of its dipole moment. Furthermore it can be readily determined by experiment. Thus the donor number may be considered as a semiquantitative indication of the solvent interaction with solutes.

C. THE PREDICTION OF DONOR–ACCEPTOR INTERACTIONS

The approximately linear relationship between the donor number of donors and the $-\Delta H_{A\cdot D}$-values of a chosen acceptor towards such donors, suggests an empirical method of predicting $-\Delta H_{A\cdot D}$-values. Calorimetric data for the interactions of A with 2 different donors are neccessary. These values are then plotted against their donor numbers. From this plot $-\Delta H_{A\cdot D}$-values towards different donors can be readily derived.

Drago and Wayland[9] have suggested an interesting method of predicting $-\Delta H_{A\cdot D}$-values according to the expression

$$-\Delta H_{A\cdot D} = C_A C_D + E_A E_D$$

where C is the covalent and E the electrostatic contribution denoted by A and D for acid and donor respectively. For the calculation the $-\Delta H$-values of A towards 4 different donors (D_1 to D_4) are measured. With

$$C_{Di} = aR_{Di}$$
$$E_{Di} = bR_{Di}$$

(R being the polarizabilities and μ the dipole moments)
four equations

$$E_A\mu_{D1}b + C_A R_{D1}a = -\Delta H_1$$
$$E_A\mu_{D2}b + C_A R_{D2}a = -\Delta H_2$$
$$E_A\mu_{D3}b + C_A R_{D3}a = -\Delta H_3$$
$$E_A\mu_{D4}b + C_A R_{D4}a = -\Delta H_4$$

are obtained, which contain 4 unknown quantities (E_A, C_A, a and b).

When C_A and E_A and the $-\Delta H_{A\cdot D}$-values towards 2 donors are known, calculations of $-\Delta H_{A\cdot D}$-values towards other donors can be carried out. With iodine and phenol, very good agreement is obtained between the observed and the calculated figures[9], whilst with trimethylboron the agreement is less satisfactory. Lack of agreement for trimethylamine has been ascribed to steric factors.

The discrepancies are appreciable when $SbCl_5$ is used as an acceptor molecule[10]. When methyl acetate and dimethylformamide are used as reference

TABLE III

CALCULATED AND OBSERVED $-\Delta H$-VALUES FOR THE REACTIONS OF $B(CH_3)_3$ TOWARDS CERTAIN N-BASES

Base	*$-\Delta H$ (calc.)*	*$-\Delta H$ (obs.)*	
NH_3		13.75	as basis for the calculations
CH_3NH_2		17.64	
$(CH_3)_2NH$	20.72	19.26	
$(CH_3)_3N$	25.82	17.62	

bases $C_{SbCl_5} = 5.17$ and $E_{SbCl_5} = 2.9$, whilst with acetone and dimethyl sulfoxide as reference bases $C_{SbCl_5} = 2.56$ and $E_{SbCl_5} = 21.70$.

TABLE 4

CALCULATIONS OF $-\Delta H_{SbCl_5 \cdot D}$ FOR DIFFERENT DONORS WITH METHYL ACETATE AND DIMETHYLFORMAMIDE AS REFERENCE DONORS

Donor	$-\Delta H_{SbCl_5 \cdot D}$	
	calculated	*observed*
CH_3CN	16.03	14.1
$(CH_3)_2CO$	12.52	17.0
$CH_3COOC_2H_5$	20.75	17.1
$(C_2H_5)_2O$	26.82	19.2
$CH_3CON(CH_3)_2$	28.41	27.8
$(CH_3)_2NCON(CH_3)_2$	28.90	29.64
$(CH_3)_2SO$	30.20	29.8
C_5H_5N	47.16	33.1

Thus the graphical approach[1,6,8] appears to be of wider applicability than the "quantitative calculation" of Drago and Wayland[9]. Both approaches require the same amount of empirical data, namely two $-\Delta H$-values representing the interaction of the acceptor towards two different donor molecules.

D. THE DONOR NUMBER AND COMPLEX FORMATION IN SOLUTION

When the formation of an anionic complex, such as a chloro-complex in a solvent is considered, the reaction occurs by addition of a competitive ligand such as Cl^- and may be represented as due to a ligand-exchange reaction, *e.g.*:

$$D\cdot SbCl_{5(\text{dissolved})} + Cl^-_{(\text{dissolved})} \rightleftharpoons [SbCl_6]^-_{(\text{dissolved})} + D$$

As may be expected the equilibrium constants, K_{complex}, of such reactions for different solvents D, were found to be inversely proportional to the donor numbers of the solvents[6–8] ($POCl_3$ is an exception).

$$DN_{SbCl_5} \cdot \log K_{\text{complex}} = \text{constant}$$

The donor number at the solvent will therefore govern the tendency of competitive ligands to form complexes since the formation of such complexes will be favoured by a decreasing ratio of the coordinating properties of solvent molecules to those of the competitive ligand. On the other hand with increasing DN_{SbCl_5} and decreasing coordinating properties of the competitive ligand ionisation will be the predominant feature for the solute in solution. With similar coordinating properties of solvent and competitive ligand, autocomplex formation may be expected to occur, at least to a certain degree[8,11].

TABLE 5

FORMATION-CONSTANTS $K_{complex}$ OF THE CHLORO-COMPLEXES FROM Ph_3CCl AND $SbCl_5$ AT CONCENTRATIONS BETWEEN 10^{-3} TO 10^{-5} M IN SOLVENTS OF DIFFERENT DN_{SbCl_5}

Solvent	DN_{SbCl_5}	$K_{complex}$
$1,2\text{-}C_2H_4Cl_2$	0.1	$> 10^5$
SO_2Cl_2	0.1	$> 10^5$
$SOCl_2$	0.4	$> 10^5$
C_6H_5COCl	2.3	$> 10^5$
$POCl_3$	11.7	$1.1 \cdot 10^2$
CH_3CN	14.1	$1 \cdot 10^3$
PDC	15.1	$3.4 \cdot 10^2$
$C_6H_5POF_2$	16.4	$1.3 \cdot 10^4$
$C_6H_5POCl_2$	18.5	$3.9 \cdot 10^1$
$(CH_3O)_3PO$	23.0	$2.5 \cdot 10^0$
$HCON(CH_3)_2$	26.6	$5.0 \cdot 10^{-2}$
$(CH_3)_2SO$	29.8	$4.0 \cdot 10^{-3}$
C_5H_5N	33.1	$< 10^{-2}$

With increasing donor number, the solvent will be increasingly useful as an ionising solvent, but the formation of complex compounds will become more difficult especially with weak competitive ligands. Since with small donor number solubility properties will in general be poor, solvents of medium donor number, such as acetonitrile ($DN_{SbCl_5} = 14$) or PDC ($DN_{SbCl_5} = 15$) are most suitable as media for numerous coordination-chemistry reactions.

E. THE DIELECTRIC CONSTANT

A high dielectric constant may be useful for an ionising solvent but this property is mainly responsible for the degree of dissociation of ionised compounds into separate ions. Despite its high dielectric constant hydrogen cyanide is a poor ionising solvent due to its low coordinating properties. On the other hand a solvent of low dielectric constant may be a very good ionising medium provided its donor properties are good, as for example is tributyl phosphate ($DN_{SbCl_5} = 24$, dielectric constant = 6.8).

F. STERIC CONTRIBUTIONS

With increasing coordination number steric consideration may become a decisive factor with bulky solvent molecules and with small acceptor molecules or ions. Thus with various transition-metal ions steric contributions may become apparent when the solvent positions in solvated metal cations are stepwise replaced by anionic ligands X^-, such as Br^-, Cl^- or N_3^-.

The interaction between VO^{2+} and the five solvent molecules is similar for both acetonitrile ($DN_{SbCl_5} = 14$) and DMSO ($DN_{SbCl_5} = 30$) because they have favourable steric properties. The interaction is weaker with propanediol-1,2-carbonate and trimethyl phosphate[12] where steric hindrance is possible. When four of the ligand positions are occupied by two acetylacetonate groups, one coordinating site is available with sufficient room for a bulky donor molecule. Thus the degree of interaction of $[VO(acac)_2]^{2+}$ with the solvents mentioned above again follows the respective donor numbers, *i.e.* DMSO > TMP > PDC > AN[10].

G. VARIOUS SYSTEMS INVOLVING TRANSITION-METAL IONS

(*i*) *General*

The consecutive replacement of solvent molecules by donor ligands in the coordination sphere of metal cations has been followed by spectrophotometric, potentiometric and conductometric techniques. The determination of the nature of the species in different solvents will indicate the occurrence of ionisation, auto-complex formation, anion-complex formation or certain structural features imposed on the complexes by solvent contributions.

Although it is impossible to draw definite conclusions which will allow us to predict the behaviour of a system in a particular solvent it may be useful to present the available results and to attempt a brief discussion from the point of view outlined above. However, metal–halide or metal–pseudohalide systems may not be the best choice, due to the various coordination forms possible, and the consecutive equilibria involved. Kinetic considerations are also important, but they have not been investigated.

The solvents used cover a reasonable range of donor numbers from acetonitrile ($DN_{SbCl_5} = 14$), propanediol-1,2-carbonate ($DN_{SbCl_5} = 15$), trimethylphosphate ($DN_{SbCl_5} = 23$), dimethylformamide ($DN_{SbCl_5} = 27$) and dimethylsulfoxide ($DN_{SbCl_5} = 30$). The coordinating properties of the competitive ligands towards group-A metals increase in the order $Br^- < Cl^- < N_3^-$.

(*ii*) *Manganese(II) systems*

In the manganese(II)–bromide system all possible coordination species are found in acetonitrile[13]. The change from octahedral to tetrahedral coordination occurs from $[MnBr]^+$ to $[MnBr_2]$ just as in the manganese(II)–chloride system in the same solvent. In PDC, manganese bromide undergoes complete auto-complex formation:

$$2\,MnBr_2 + 6\,PDC \rightleftharpoons \underset{\text{octahedral}}{[Mn(PDC)_6]^{2+}} + \underset{\text{tetrahedral}}{[MnBr_4]^{2-}}$$

Tetrahedral $[MnCl_4]^{2-}$ is formed in acetonitrile but not in propanediol-1,2-carbonate, indicating the stronger interaction of Mn^{II} with PDC[14]. Indeed towards Mn^{II} PDC behaves intermediate in donor strength between AN and TMP, the latter having a higher donor number and favouring the formation of octahedral coordination species. The formation of the chloro-compounds in TMP is much slower than in PDC due to the relatively-high kinetic stability of the species with low Cl^- coordination number[14]. The bromide ion is too weak a ligand in comparison to TMP, to form any bromo-complexes in this solvent[13]. Thus manganese(II) bromide is ionised in TMP, even in the presence of excess bromide ions, just as occurs in dimethyl sulfoxide[13].

$$MnBr_2 + 6\,TMP \rightleftharpoons \underset{\text{octahedral}}{[Mn(TMP)_6]^{2+}} + 2\,Br^-$$

$$MnBr_2 + 6\,DMSO \rightleftharpoons \underset{\text{octahedral}}{[Mn(DMSO)_6]^{2+}} + 2\,Br^-$$

TABLE 6

MANGANESE(II) SYSTEMS

Species	*Solvent*			
	AN	*PDC*	*TMP*	*DMSO*
$[MnBr]^+$	+	−	−	−
$[MnBr_2]$	+	−	−	−
$[MnBr_3]^-$	+	−	−	−
$[MnBr_4]^{2-}$	+	+	−	−
$[MnCl]^+$	+	−	−	
$[MnCl_2]$	+	+	+	
$[MnCl_3]^-$	−	−	−	
$[MnCl_4]^{2-}$	+	−	+	
$[MnCl_6]^{4-}$	−	?	?	
$[Mn(N_3)]^+$	−	−	−	
$[Mn(N_3)_2]$	+	+	+	
$[Mn(N_3)_3]^-$	−	−	−	
$[Mn(N_3)_4]^{2-}$	+	+	?	
$[Mn(N_3)_6]^{4-}$	−	−	?	

Thus, towards Mn^{II} the bromide ion is a stronger ligand than AN comparable in donor strength to PDC and definitely weaker than TMP or DMSO, whilst the donor strength of the chloride ion towards Mn^{II} may lie between those of TMP and DMSO.

Only tetrahedral azido complexes are formed in AN and PDC while in solutions of TMP the octahedral diazide and an octahedral azidomanganate(II) ion is preferred.

(*iii*) *Cobalt(II) systems*

TABLE 7

COBALT(II) SYSTEMS

Species	*Solvent*					
	AN	*PDC*	*Me$_2$CO*	*TMP*	*DMF*	*DMSO*
$[CoBr]^+$	+	−	−	+		−
$[CoBr_2]$	+	−	+	+		−
$[CoBr_3]^-$	+	−	+	+		−
$[CoBr_4]^{2-}$	+	+	+	+		−
$[CoCl]^+$	−		−	−	+	−
$[CoCl_2]$	+		+	+	+	?
$[CoCl_3]^-$	+		+	+	+	−
$[CoCl_4]^{2-}$	+		+	+	+	+
$[CoN_3]^+$	−			+		−
$[Co(N_3)_2]$	+			+		+
$[Co(N_3)_3]^-$	−			−		−
$[Co(N_3)]_4^{2-}$	+			+		+

Towards Co^{2+} the bromide ion seems to be comparable in donor strength to PDC[15], which gives rise to autocomplex formation in its solution. $CoBr_2$ gives a pink solution at once in DMSO since it is completely ionised[15]:

$$CoBr_2 + 6\,DMSO \rightleftharpoons \underset{\text{octahedral}}{[Co(DMSO)_6]^{2+}} + 2\,Br^-$$

Excess of bromide ions will not lead to the formation of a bromo-complex. The more-strongly coordinating Cl^- ions readily give chloro-complexes in AN and TMP[16] and are comparable with the coordinating properties of DMSO towards Co^{II}, where auto-complex formation occurs[17]:

$$CoCl_2 + 6\,DMSO \rightleftharpoons \underset{\text{octahedral}}{[Co(DMSO)_6]^{2+}} + \underset{\text{tetrahedral}}{[CoCl_4]^{2-}}$$

$CoCl^2$ is undissociated in nitromethane[17a] ($DN_{SbCl_5} \sim 8$), autocomplex in acetonitrile ($DN_{SbCl_5} = 14.1$) acetone[17b] ($DN_{SbCl_5} \sim 17$) as well as in TMP, DMF and DMSO with decreasing stabilities of the anionic complex ions.

Cobalt azide is also subjected to autocomplex formation in solution of dimethyl sulfoxide. It might be expected that $CoCl_2$ and $Co(N_3)_2$ will undergo ionisation in a solvent of still higher DN_{SbCl_5}.

The species $[CoBr]^+$ found in AN and TMP and $[CoN_3]^+$ found in TMP are octahedral. In the cobalt(II)-chloride system no analogous species were found, although $[CoCl]^+$ is known to exist in aqueous solutions[18,19]. All higher coordinated forms show tetrahedral structures in AN, PDC and DMSO. The change from octahedral to a tetrahedral species takes place when the second competitive ligand is added to give the neutral species CoX_2D_2, which has a slightly distorted tetrahedral structure.

(*iv*) *Nickel(II) systems*

TABLE 8

NICKEL(II) SYSTEMS

Species	*Solvent*				
	AN	*PDC*	*TMP*	*DMF*	*DMSO*
$[NiBr]^+$	+	−	−		−
$[NiBr_2]$	+	−	+		−
$[NiBr_3]^-$	+	−	−		−
$[NiBr_4]^{2-}$	+	+	+		−
$[NiCl]^+$			−	+	−
$[NiCl_2]$			+	−	−
$[NiCl_3]^-$			+	+	−
$[NiCl_4]^{2-}$			+	−	−
$[Ni(N_3)]^+$	−		−		−
$[Ni(N_3)_2]$	+		+		+
$[Ni(N_3)_3]^-$	−		−		−
$[Ni(N_3)_4]^{2-}$	+		?		+
$[Ni(N_3)_6]^{4-}$			?		−

TMP however, differs as a solvent, since tetrahedral species are converted to octahedral or pseudo-octahedral species in its solutions[20].

Auto-complex formation occurs with nickel(II) and Br^- ions in PDC[15], with Cl^- ion in the more-strongly coordinating DMF[21] and with N_3^- ion at least in part in DMSO[20]. Both $NiBr_2$ and $NiCl_2$ are simply ionised in DMSO with no indication of formation of chloro-complexes in the presence of excess chloride ion

$$NiBr_2 + 6\ PDC \rightleftharpoons \underset{\text{octahedral}}{[Ni(PDC)_6]^{2+}} + \underset{\text{tetrahedral}}{[NiBr_4]^{2-}}$$

$$NiBr_2 + 8\ TMP \rightleftharpoons [Ni(TMP)_6]^{2+} + [NiBr_4(TMP)_2]^{2-}$$

$$NiBr_2 + 6\ DMSO \rightleftharpoons [Ni(DMSO)_6]^{2+} + 2\ Br^-$$

$$NiCl_2 + 6\ DMSO \rightleftharpoons \underset{\text{octahedral}}{[Ni(DMSO)_6]^{2+}} + 2\ Cr^-$$

Trimethyl phosphate ($DN_{SbCl_5} = 23$) exhibits unique properties towards Ni^{II} in as much as pseudo-octahedral coordination occurs towards the bromide ion.

Additional solvent contributions account for the fact that in TMP the hexa-coordination of the solvated nickel(II) ion is maintained by stepwise azide coordination with the probable formation of a hexaazido complex ion. The stability of $Ni(N_3)_2$ is low compared with that of the hexaazidonickel(II) ion, indicating some autocomplex formation of $Ni(N_3)_2$ in this solvent.

In acetonitrile a change to the diazide is found. In this solvent hexacoordinated species $[Ni(N_3)_a(AN)_{6-a}]^{+2-a}$ are again present.

In DMSO the azido complexes show lower stabilities than in AN since reasonable competition is provided by the strongly-coordinating solvent molecules[20]. The species $[Ni(N_3)_4]^{2-}$ seems to have a distorted octahedral arrangement with two DMSO molecules coordinated at the apices of the octahedron. Thus $[Ni(N_3)_4]^{2-}$ may be considered as planar with respect to azide coordination, just as is known in $[Ni(CN)_4]^{2-}$.

The preferred hexa-coordinated arrangements in the azido complexes in all three solvents may be favoured by the small size of the rod-like azide ions and by π-bonding contributions in the metal–azide bonds.

(*v*) *Copper(II) systems*

TABLE 9

COPPER(II) SYSTEMS

Species	*Solvent*			
	AN	*TMP*	*DMF*	*DMSO*
$[CuCl]^+$	+	+	+	+
$[CuCl_2]$	+	+	−	+
$[CuCl_3]^-$	+	+	+	−
$[CuCl_4]^{2-}$	+	+	−	−
$[Cu(N_3)]^+$	+	+		+
$[Cu(N_3)_2]$	+	+		+
$[Cu(N_3)_3]^-$	+	+		−
$[Cu(N_3)_4]^{2-}$	+	+		+

In the copper(II) system in acetonitrile and trimethyl phosphate all possible coordination forms with chloride[16,22] and azide are found[20]; autocomplex formation occurs for $CuCl_2$ in DMF[21] ($DN_{SbCl_5} = 27$) while ionization of $CuCl_2$ takes place in the more strongly coordinating dimethyl sulfoxide even in the presence of excess chloride ions.

In the copper(II)–azido system, $[CuN_3]^+$, $Cu(N_3)_2]$, $[Cu(N_3)_3]^-$ and $[Cu(N_3)_4]^{2-}$ are found in TMP and AN. In DMSO, $[CuN_3]^+$, $[Cu(N_3)_2]$ and $[Cu(N_3)_4{}^-]$ may be formed. All azido-complexes have distorted-tetrahedral structures as is characteristic for Cu^{II}. The stability of the azido-complexes in DMSO is higher than that of corresponding chloro-complexes in the same solvent, where there is stronger competition between chloride ion and DMSO molecules as ligands.

(*vi*) *Vanadium(III) systems*

VCl_3 and VBr_3 give colored solutions in AN in which six-coordinated units $VX_3 \cdot (AN)_3$ were shown to be present[23]. Several X^--coordinated species are found in AN and TMP with some indication of partial dissociation of the tetrahalo-

TABLE 10

VANADIUM(III) SYSTEMS

Species	Solvent		
	AN	PDC	TMP
$[VBr]^{2+}$	−	−	+
$[VBr_2]^+$	+	−	−
$[VBr_3]$	+	−	+
$[VBr_4]^-$	+	+	−
$[VCl]^{2+}$	−	+	+
$[VCl_2]^+$	−	−	−
$[VCl_3]$	+	+	+
$[VCl_4]^-$	+	+	−
$[V(N_3)]^{2+}$	+	+	+
$[V(N_3)_2]^+$	−	−	−
$[V(N_3)_3]$	+	+	+
$[V(N_3)_4]^-$	−	+	−
$[V(N_3)_6]^{3-}$	+	+	−

complexes[24]; this is more pronounced in the strongly-coordinating DMSO.

Although acetonitrile and propanediol-1,2-carbonate have nearly-identical donor numbers, complexes of low coordination number towards halide and pseudohalide ions show higher stabilities in AN. In the bromide system autocomplex formation occurs in PDC[13], while partial ionization of VBr_3 occurs in TMP.

$$(TMP)_3VBr_3 + 2\,TMP \rightleftharpoons [(TMP)_5VBr]^+ + 2\,Br^-$$

Again TMP is unique in that even the octahedral triazide has a low solubility and shows no marked tendency to further N_3^--coordination[24]. This is likely to

(vii) Titanium(III) systems

TABLE 11

TITANIUM(III) SYSTEMS

Species	Solvent		
	AN	PDC	TMP
$[TiCl]^{2+}$	−	+	−
$[TiCl_2]^+$	−	−	+
$[TiCl_3]$	+	+	+
$[TiCl_4]^-$	+	+	?
$[TiCl_6]^{3-}$	−	+	−
$[Ti(N_3)]^{2+}$	−	−	−
$[Ti(N_3)_2]^+$	−	−	+
$[Ti(N_3)_3]$	+	+	+
$[Ti(N_3)_4]^-$	+	−	+
$[Ti(N_3)_6]^{3-}$	+	+	−

be due the presence of polymeric and possibly partially-solvated species, suggested by the poor solubility and the tendency to form colloidal solutions[24].

The tendency for hexacoordination with a distorted-octahedral structure is observed for titanium(III) compounds, where cationic species are hardly detected[24,25]. The neutral species TiX_3 are non-electrolytes in AN where they are six-coordinated, and in TMP polymeric species seem to be present. In PDC both hexachloro- and hexaazido species seem to be formed; the latter is also formed in AN.

In AN $[Ti(N_3)_4]^-$ is found as an intermediate in the formation of the hexaazido complex[25], while in PDC there are no indications of the tetraazido compound.

(viii) *Chromium(III) systems*

TABLE 12

CHROMIUM (III) SYSTEMS

Species	*Solvent*		
	AN	*PDC*	*TMP*
$[CrCl]^{2+}$	−	−	+
$[CrCl_2]^+$	+	+	−
$[CrCl_3]$	+	+	+
$[CrCl_4]^-$	+	+	+
$[CrCl_6]^{3-}$	+	−	−
$[Cr(N_3)]^{2+}$	−	−	+
$[Cr(N_3)_2]^+$	+	+	−
$[Cr(N_3)_3]$	+	+	+
$[Cr(N_3)_4]^-$	−		−
$[Cr(N_3)_6]^{3-}$	+	+	−

As may be expected for Cr^{III}, only hexacoordinated forms[27] are present in this system[24,25]. Again the highest chloro- and azido-complexes are not formed in TMP, due to factors indicated in the discussion for Ti^{III} and V^{III} compounds. In AN and PDC the cationic species $[CrX_2D_4]^+$ is formed in equilibrium with both $[Cr(D)_6]^{3+}$ and CrX_3D_3.

(ix) *Iron(III) systems*

The results obtained in the iron(III) systems again provide evidence that the coordinating properties of both the solvent and the competitive ligand are very important. Thus in DMSO, a solvent of high DN_{SbCl_5}, no chloro-complexes of ferric ion can be detected[17,28] since DMSO is a stronger ligand than the chloride ion. Accordingly no bromo- and iodo-complexes can be expected to be formed in this solvent apart from the instability of such iron(III)-systems towards redox reactions. With azide ion — a ligand which is stronger than the chloride ion — only octahedral $[Fe(N_3)_4]^-$ can be detected[29], indicating autocomplex formation of the assumed triazide just as has to be assumed for ferric fluoride in the same solvent. With stronger ligands such as SCN^-, stronger complexes with higher coordination numbers can be found even in DMSO[29].

Both chloro- and azido-complexes can be formed in solvents of lower DN_{SbCl_5} such as AN or PDC, while in DMSO $[Fe(N_3)_4(DMSO)_2]^-$ is the highest anionic species.

While $FeCl_3$ is completely dissociated in the strongly-coordinating DMSO even in the presence of a large excess of chloride ion, autocomplex formation is favoured both in TMP[30] and triethyl phosphate[31]. The formation of chloro complexes is preferred in solvents of lower DN_{SbCl_5} even if only small amounts of chloride ions are present, as seems to occur in phosphorus oxychloride[32,33] or phenylphosphonic dichloride[34]. Indeed $POCl_3$ and $(EtO)_3PO$ have vastly-different coordinating properties and any conclusions drawn from the results in triethyl phosphate cannot be applied to a different solvent such as $POCl_3$ as has been

TABLE 13

IRON(III) SYSTEMS

Species	*Solvent*					
	POCl₃	*AN*	*PDC*	*TMP*	*DMA*	*DMSO*
$[FeCl]^{2+}$		+	+	−		−
$[FeCl_2]^+$		−	−	+	+	−
$[FeCl_3]$	+	+	+	+	+	−
$[FeCl_4]^-$	+	+	+	+	+	−
$[Fe(N_3)]^{2+}$		−	+	−		−
$[Fe(N_3)_2]^+$		−	+	−		−
$[Fe(N_3)_3]$		+	+	+		−
$[Fe(N_3)_4]^-$		−	−	−		+
$[Fe(N_3)_6]^{3-}$		+	+	+		−
$[FeF]^{2+}$						−
$[FeF_2]^+$						+
$[FeF_3]$						−
$[FeF_4]^-$						+
$[FeF_6]^{3-}$						−
$[Fe(CN)]^{2+}$						−
$[Fe(CN)_2]^+$						+
$[Fe(CN)_3]$						+
$[Fe(CN)_4]^-$						+
$[Fe(CN)_6]^{3-}$						−
$Fe(SCN)_3$						−
$Fe(SCN)_6$						+

recently advanced[35,36]. In the latter solvent considerable association of $FeCl_3$ is observed as well as in the weakly coordinating solvent nitromethane[37].

It is remarkable that in all the solvents investigated, no octahedral chloro complexes have been found — even in TMP tetrahedral $[FeCl_4]^-$ ions being present[30]. The change from octahedral $[FeL_6]^{3+}$ to tetrahedral species occurs with the coordination of the first chloride ion; $[FeCl]^{2+}$ is clearly tetrahedral in AN and PDC[14].

(x) *Vanadyl(IV) systems*

TABLE 14

VANADYL(IV) SYSTEMS

Species	*Solvent*				
	AN	*PDC*	*H_2O*	*TMP*	*DMSO*
$[VOCl]^+$	+	+	+	−	+
$[VOCl_2]$	+	+	+	+	−
$[VOCl_3]^-$	−	+		?	−
$[VoCl_4]^{2-}$	+	+	+	+	−
$[VOCl_5]^{3-}$	−	−		−	−
$[VO(N_3)]^+$	+	+		−	+
$[VO(N_3)_2]$	+	+		+	+
$[VO(N_3)_3]^-$	−	−		−	
$[VO(N_3)_4]^{2-}$	−	−	+	?	
$[VO(N_3)_5]^{3-}$	+	+		+	+

A difference between the chloro- and azido-systems of vanadyl(IV) is the formation of $[VOCl_4]^{2-}$ as the highest anionic complex in all solvents investigated whilst $[VO(N_3)_5]^{3-}$ appears to be present under similar conditions. The highest forms are produced in AN and PDC with stoichiometric amounts of the ligand ion, whilst in TMP a tenfold excess and in DMSO a 150-fold excess of ligand is necessary for the azido complexes[37]. This is again an indication of the importance of the relative coordinating properties of solvent molecules and of the competitive ligands.

The greater coordinating strength of the azide ion is clearly shown in DMSO, where dissociation of $VOCl_2$ takes place even in the presence of excess chloride ions[12]

$$VOCl_2 + n\ DMSO \rightleftharpoons [VOCl(DMSO)_n]^+ + Cl^-$$

$$[VOCl(DMSO)_n]^+ + SbCl_5DMSO \rightleftharpoons [VO(DMSO)_{n+1}]^{2+} + [SbCl_6]^-$$

On the other hand with azide ions an anionic azido complex is formed in solutions of DMSO.

TABLE 15

VANADYL(IV) PERCHLORATE SPECTRA IN DIFFERENT SOLVENTS

Solvent	*Maximum (nm)*	*Shoulders (nm)*
an	785	675
PDC	680	(700)
H_2O	765	625
TMP	720	820, 785, 550, 380
DMSO	825	625

A consideration of the electronic spectra of vanadyl(IV) perchlorate in AN PDC, TMP and DMSO shows the contribution by the solvent molecules as seen in Table 15.

In solvents of low- and of high donor numbers, namely AN and DMSO respectively, the maximum is found at long wavelength and the shoulder at smaller wavelength, while in solvents of intermediate DN_{SbCl_5}, namely PDC and TMP the reverse is true. Thus the steric factor appears to determine the degree of ion–solvent interaction: the small size of the AN-molecules favours stronger interaction than with PDC or TMP[38].

H. CONCLUSIONS

The discussion above shows that, in a qualitative way, the order of the donor strengths of the solvents is usually invariant but steric contributions are also important.

Acetonitrile with its medium donor number, reasonably high dielectric constant and favourable steric properties gives rise to most of the possible coordination species which are of course in equilibrium.

Propanediol-1,2-carbonate, similar in donor number to AN but with high dielectric constant and less-favourable steric properties gives rise to auto-complex formation in certain bromide systems showing an interaction with the metal cations which is stronger than that of AN. Sometimes octahedral forms are favoured, while in AN the corresponding species have tetrahedral arrangements.

TMP of stronger coordinating properties favours hexacoordination (only Co^{II} and Fe^{III} giving tetrahedral species in this solvent). Autocomplex formation is found in some bromo- and chloro-systems and possibly also in the nickel(II)–azido system. The number of coordination forms established in the solutions is in general smaller than in AN or PDC, some of lower-coordinated forms show high kinetic stabilities. Hexachloro- and hexaazido complexes are usually easily formed, but with Ti^{III}, V^{III} and Cr^{III} complexes, of the type $M(N_3)_3$ are extraordinarily stable; this is probably due to the formation of polymeric species. The tendency to form macromolecular species is an example of a specific solvent effect which has not been investigated in any more detail.

In DMF, a still-stronger coordinating solvent ($DN_{SbCl_5} = 27$), autocomplex formation is indicated for $NiCl_2$, $CuCl_2$ and $FeCl_3$ which will show ionisation in DMSO ($DN_{SbCl_5} = 30$).

DMSO, the strongest donor solvent under consideration, ionises many halides without any possibility of giving anionic complexes even in the presence of a large excess of halide ion; examples include $CoBr_2$, $MnBr_2$, $CuCl_2$, $NiCl_2$, $FeCl_3$, $VOCl_2$ and SnI_4[39]. With stronger ligands such as N_3^- or CN^-, and Fe^{III} ion, hexacoordinated forms containing solvent molecules as ligands are preferred, *e.g.* $[Fe(N_3)_4(DMSO)_2]$ being the highest azide complex.

It will be of interest to extend the investigations to other transition-metal systems and to other solvents, to measure the coordinating properties of various competitive ligands and the acceptor strength of various metal cations.

REFERENCES

1 V. Gutmann, A. Steininger and E. Wychera, *Monatsh.*, 97 (1966) 460.
2 V. Gutmann and U. Mayer, *Monatsh.*, 98 (1967) 294.
3 V. Gutmann, E. Wychera and F. Mairinger, *Monatsh.*, 97 (1966) 1265.
4 V. Gutmann, E. Wychera and S. Angelov, unpublished work.
5 T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, 88 (1966) 3921.
6 V. Gutmann and E. Wychera, *Inorg. Nucl. Chem. Letters*, 2 (1966) 257.
7 V. Gutmann and E. Wychera, Revue de Chimie Minérale.
8 V. Gutmann, to be published by Cambridge University Press.
9 R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, 87 (1965) 3751.
10 V. Gutmann and U. Mayer, unpublished work.
11 M. Baaz and V. Gutmann, in G. Olah (Ed.), *Friedel-Crafts and Related Reactions*, Vol. I Interscience, New York, 1963, p. 357.
12 V. Gutmann and H. Laussegger, *Monatsh.*, in press.
13 V. Gutmann and K. Fenkart, *Monatsh.*, 98 (1967) 286.
14 V. Gutmann and W. Lux, Monatsh., in press.
15 V. Gutmann and K. Fenkart, *Monatsh.*, 98 (1967) 1.
16 M. Baaz, V. Gutmann, G. Hampel and J. R. Masaguer, *Monatsh.*, 93 (1962) 1416.
17 V. Gutmann and L. Hübner, *Monatsh.*, 92 (1961) 1261; 17a S. Buffagny and T. M. J. Dunn, *J. Chem. Soc.*, (1961) 5105; 17b J. A. Fine, *J. Am. Chem. Soc.*, 82 (1965) 1139; S. Sramko, *Chem. Abstr.*, 60 (1964) 8697b.
18 P. Job, *Ann. Chim.*, II 6 (1936) 97.
19 H. L. Schläfer and H. P. Opitz, *Z. Elektrochem.*, 65 (1961) 372.
20 V. Gutmann and O. Leitmann, *Monatsh.*, 97 (1966) 926.
21 H. Hubacek, B. Stancic and V. Gutmann, *Monatsh.*, 94 (1963) 1118.
22 V. Gutmann, G. Hampel and J. R. Masaguer, *Monatsh.*, 94 (1963) 822.
23 R. J. H. Clark, R. S. Nyholm and D. E. Scaife, *J. Chem. Soc.*, (1966) 1296.
24 V. Gutmann, O. Leitmann, H. Czuba and A. Scherfhaufer, *Monatsh.*, 98 (1967) 188.
25 V. Gutmann, A. Scherhaufer and H. Czuba, *Monatsh.*, in press.
26 R. J. H. Clark, J. Lewis, D. J. Machin and R. S. Nyholm, *J. Chem. Soc.*, (1963) 379.
27 C. K. Jørgensen, in A. Hemer *Advan. Chem. Ser.*, *Centennial Symp. Vol.* (1966).
28 V. Gutmann and G. Hampel, *Monatsh.*, 94 (1963) 830.
29 B. Csiszar, V. Gutmann and E. Wychera, *Monatsh.*, 98 (1967) 12.
30 V. Gutmann and W. Lux, *J. Inorg. Nucl. Chem.*, in press.
31 D. W. Meek and R. S. Drago, *J. Am. Chem. Soc.*, 83 (1961) 4322.

32 M. BAAZ, V. GUTMANN AND L. HÜBNER, *Monatsh.*, 91 (1960) 537, 694.
33 M. BAAZ, V. GUTMANN AND L. HÜBNER, *J. Inorg. Nucl. Chem.*, 18 (1961) 276.
34 M. BAAZ, V. GUTMANN AND L. HÜBNER, *Monatsh.*, 93 (1961) 135.
35 R. S. DRAGO AND K. F. PURCELL, *Progr. Inorg. Chem.*, 6 (1964) 271.
36 R. S. DRAGO AND K. F. PURCELL, in T. C. WADDINGTON (Ed.), *Non-Aqueous Solvent Systems*, Academic Press, London-New York, 1965, p. 213.
37 P. A. D. DE MAINE AND E. KOUBEK, *J. Inorg. Nucl. Chem.*, 11 (1959) 329.
38 J. SELBIN AND T. R. ORTOLANO, *J. Inorg. Nucl. Chem.*, 26 (1964) 37.
39 F. GAIZER AND T. M. BECK, *J. Inorg. Nucl. Chem.*, 29 (1967) 21.