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On the Coordinating Properties of some Solvents. A Vibrational Spectroscopic Study of Mercury(II) Halides and Antimony(V) Chloride in Solution; New Concepts for Lewis Basicity Scales of Solvents

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Abstract

Raman and infrared spectra of the stretching vibrational frequencies of mercury(II) halides in solvents with widely different solvating abilities, have been recorded and combined with literature data. The frequencies decrease as the interaction of the solvent with the mercury atom in the HgX_2 entity increases. Using published data from structure determinations by X-ray diffraction in solutions and crystals, an empirical correlation of the XHgX angle and the frequency shift is obtained.

An empirical scale ranking the donor strength towards a soft acceptor is proposed for more than sixty solvents with widely varying solvating properties. The numerical donor strength D_S values have been obtained as the decrease in the symmetric stretching vibration frequency of the $HgBr_2$ molecule between the gas phase and solution. This D_S scale is compared with some previously proposed scales, determined with the use of hard or borderline acceptors. The most well-known of these, the donor number D_N scale based on enthalpy data of the adduct formation $SbCl_5 \cdot L$ (L = solvent molecule) in 1,2-dichloroethane is also compared with Raman measurements of the Sb–Cl stretching frequencies of the $SbCl_5 \cdot L$ adducts in this solvent. The dependence of the measured donor strength of the solvent molecules on the properties of the acceptor and on the method used for the donor classification is discussed. An additional donor strength scale D_H for hard acceptors is derived for 24 solvents from published data. The scale is based on Gibb's free energy of transfer of the sodium ion from a solvent to a reference solvent (1,2-dichloroethane). There is hardly any correlation between the soft D_S and the hard D_H scales, while the D_S and D_N scales show a fair agreement for solvents with hard donor atoms.

Introduction

In recent years several papers have dealt with the solvation of mercury(II) halides in solvents with different coordinating properties [1–9]. Those which have sought correlations between vibrational spectra and solvation have concentrated on non-donor, O-donor and N-donor systems. Discussions have centred on the behaviour of symmetric stretching modes ν_s of $HgCl_2$ and $HgBr_2$ species, because in only a minority of cases have the asymmetric stretching frequencies ν_{as} been determined.

Mercury(II) is a typical soft electron pair acceptor forming strong bonds with covalent character to soft donor atoms. Most of the available data for solvated mercury(II) halides concern solvents with hard donor atoms. In the present study we have examined a range of solvents with soft donor atoms (mainly N, S and P). More extensive IR studies have enabled us to document ν_{as} modes more fully than hitherto.

In a series of separate studies, with X-ray diffraction on HgX_2 solutions (X = Cl, Br or I), we found increasing Hg–X bond lengths and decreasing XHgX angles for the solvated HgX_2 species in the solvents methanol, dimethylsulfoxide (DMSO), pyridine (py) and tetrahydrothiophene (THT), in that order [10–13]. These findings are used in combination with the present results to discuss the nature of solvation, explore the correlation between XHgX angles and vibrational frequencies and propose a relative scale of solvent donor abilities based on the response between vibrational frequencies and solvation of the $HgBr_2$ species.

Lewis acid–base interactions play a very important role in most chemical reactions in solution. Thus, any principle which allows predictions of the strength of donor–acceptor relations is of great interest and a

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large number of more or less successful attempts to find such relations has been made. Correlations with bulk solvent properties such as dielectric constant, dipole moment, proton acidity or basicity, stability or rate constants or hydrogen bonding ability have only a limited applicability. Precise quantum-mechanical calculations of the energy of adduct formation are not yet generally feasible, and therefore empirical rankings of the donor and acceptor strengths still have to suffice [14–17]. Several classifications have been proposed relating a measurable property of the solution to the solvating ability of the solvent. A tangible effect is the heat of a donor–acceptor reaction, which has been used as a basis for several scales. One of the most well-known is Gutmann's 'donor numbers' D_N, defined as the enthalpy for the 1:1 adduct formation between the donor molecule L and the chosen reference acceptor $SbCl_5$ for dilute solutions in the inert medium 1,2-dichloroethane, $SbCl_5 + L \rightarrow SbCl_5 \cdot L$ [18–21]. Although both the concept and some experimental values have been criticized [16, 17, 22], this scale is often used in comparisons with more recent proposals.

A principally similar enthalpy-based scale is the one given by Maria and Gal [16]. They chose BF_3 in dilute solutions of dichloromethane as the reference acceptor, because it gives a smaller number of side reactions than $SbCl_5$.

Drago has separated the enthalpy change on adduct formation, mainly involving iodine and phenol in gas phase or in poorly coordinating solvents, into two terms [17]. The acid and the base are each characterized by two independent parameters, *E* and *C*, which originally were described as being related to their ability to participate in electrostatic and covalent bonding, respectively. This method works best for weakly interacting adducts, but fails for many strongly interacting systems [14].

Moreover, all of the calorimetric methods mentioned above rely on the assumptions that the entropy contributions are approximately constant and that the adducts are of a 1:1 stoichiometry, in order to be able to relate the enthalpy change to the adduct bond strength. The influence of the diluting inert medium is also assumed to be negligible, although the solvation of, or the interactions between, the dissolved species could be different from that in the pure solvent [23].

In order to study the strength of the donor–acceptor interactions in the donating solvent it seems in principle preferable to measure a change in a molecular property on the interaction or adduct formation. The recent development of spectroscopic techniques has dramatically improved the feasibility of such studies and a number of scales for classifications of solute–solvent interactions has appeared [14, 15, 24]. Visible and UV spectrometry, NMR chemical shifts and vibrational frequency shifts have been used with various degrees of completeness and correlation among the solvent scales. Generally only a restricted range of solvents is encompassed because of side reactions with the solute or lack of solubility.

Among several solvatochromic scales the 'solvent polarity' described by the *Z* values of Kosower, based on the shift of an absorption band in 1-alkylpyridiniumiodide solutions, and the E_T values of Dimroth and Reichardt derived from the change in a charge-transfer band in pyridinium-*N*-phenolbetaines, cover a large range of solvents [15]. They correlate well with each other but not with Gutmann's donor numbers (better with Gutmann's acceptor numbers) and are evidently a measure of different properties of the solvent. Dipole–dipole interactions seem to be the dominant contribution [15, 21, 22]. Other solvent donor scales, determined for acceptors with defined ligand sites do, however, correlate well with for example Gutmann's donor numbers. A recent scale also useful for demonstration purposes is the one described by Sone and Fukuda, based on the solvent effects on the colour of the copper(II) *N,N,N',N'*-tetramethylenediamine acetylacetonate complex, $Cu(tmen)(acac)^+$ [25, 26].

In contrast to the assumption inherent in Gutmann's single scale of basicity order [21], it has since long been recognized that the donor properties of the solvents depend on the specific properties of the acceptor. This is qualitatively described in Pearson's hard–soft acid–base principles, in the division of acceptors into class a and b by Ahrland *et al.*, and empirically accounted for in Drago's *E* and *C* parameter concept [14].

It is, however, not yet possible to make a universal concept of this type without numerous exceptions from the rule and therefore we here propose two contrasting scales of the donor properties of solvents. The first and most complete is the D_S scale, based on the vibrational shifts of the $HgBr_2$ entity in solution, and is valid for a soft acceptor capable of forming bonds with a high degree of covalency. The second, the D_H scale, is an attempt to approach the other extreme of the acceptor properties. The free energy of transfer of the hard sodium ion from the solvent to 1,2-dichloroethane is used as a means of ranking donor abilities of solvents for mainly electrostatic donor–acceptor interactions.

In order to obtain a direct comparison of an enthalpy based scale and a scale derived from vibrational shifts, the symmetric stretching frequencies of the adduct $SbCl_5 \cdot L$ in 1,2-dichloroethane were recorded for some solvents L and compared with Gutmann's donor numbers.

Experimental

Chemicals

The mercury(II) chloride, bromide and iodide (red) were recrystallized from hot water, ethanol and acetone, respectively. Most solvents were freshly distilled prior to use as described in the literature [27]. The antimony(V) chloride (Riedel–DeHaen AG) was used without further purification.

Vibrational Spectra

Infrared spectra were measured with a Nicolet 7199A FT-IR spectrometer using a 6.25 μm mylar beam splitter (effective spectral range 100–500 cm^{-1}), Globar source and polyethylene-windowed DTGS detector. Sample thicknesses were chosen on the basis of the concentrations attainable and solvent absorption characteristics. Most measurements were performed at 4 cm^{-1} resolution using cells of thickness 0.2 mm (high density polyethylene windows) and concentrations of about 0.2 mol dm^{-3}. The very dilute solutions attainable in 1,2-dichloroethane or benzene were measured at 0.9 mm thickness. Measurements in the strongly absorbing solvents water, methanol, dimethylacetamide and tributylphosphate, as well as those of $HgCl_2$ in acetone and acetonitrile, were performed with concentrated solutions (up to 2 mol dm^{-3}) at 12 μm thickness between silicon windows.

Raman spectra were excited with a Coherent Radiation Laboratories Innova Argon laser using the 514.5 nm line at an effective power of approximately 500 mW at the sample. Spectra were recorded with a DILOR RTI triple monochromator using DC amplification with a spectral bandwidth of 4 cm^{-1}. The spectra were recorded for saturated solutions, in some cases the solutions were diluted and rerecorded without any observable changes in the mercury–halide frequencies. Iodides give the most intense Raman features whereas chlorides give the most intense infrared effects. Band positions are estimated to be accurate within 1 cm^{-1}.

Results

Solvation of HgX_2

The stretching frequencies (ν_s and ν_{as}) of the HgX_2 entities in solution are listed in Table I, which includes the gas phase values and some other solution values from the literature.

The stretching frequencies of HgX_2 in solution are sensitive to the nature and strength of the solvent interaction. Although benzene, dichloromethane and 1,2-dichloroethane are not expected to coordinate in any classical sense, they give rise to values that are lower than those obtained in the gas phase. Any interaction with these solvents is presumably by van der Waals forces. This group of solvents, noncoordinating relative to HgX_2, also includes the hard O-donor solvents nitromethane, nitrobenzene, furan, and anisole (methylphenylether), which all show practically the same frequency shift as benzene (Table I). It seems likely that these do not form any discrete bonds to mercury. Unsymmetrical association can cause breakdown of the $D_{\infty h}$ selection rules permitting ν_s to become IR active and ν_{as} to become Raman active, but no such evidence is seen.

For the O-donors acetic acid, methylacetate, propylene carbonate, diethylether, tetramethylene sulfone, acetone and γ-butyrolactone, there is a marked frequency lowering, and for a few members of this set ν_{as} has been reported as a very weak feature in Raman spectra. The quality of the IR spectra of the $HgCl_2$ solutions in propylene carbonate and diethylether was sufficient for very weak bands at the position of ν_s to be observed.

The alcohols methanol, ethanol, 1-butanol, and 1,2-ethanediol form a group of O-donors with somewhat stronger interaction with mercury(II). The behaviour of water is slightly out of line with ν_{as} values especially for $HgCl_2$ being markedly lower than the values found for the other members of this set; a possible explanation could be hydrogen-bonding to the bound halide atoms. Similar intermediate effects are obtained with the cyclic ethers tetrahydrofurane and 1,4-dioxane, and with formaline, tri-n-butylphosphate and trimethylphosphate, while the sulfoxides give the lowest frequencies of the pure O-donor solvents. Even for the most powerful of the O-donor solvents only weak features are seen that can be attributed to the breakdown of the selection rules for a linear HgX_2 skeleton.

Amongst N-donor solvents, the nitriles are the weakest donors with alkylnitriles acetonitrile, propionitrile and n-butyronitrile, similar to the O-donor acetone. The mercury halides are only sparingly soluble in tertiary amines, which limits what we can observe, but the solubility increases in primary and secondary amines [23]. Dibutylamine dissolves all three mercury(II) halides, and displays spectra for the iodide and bromide of a somewhat different type than any of those described above. The infrared spectra show two separate bands, with the ν_{as} feature not very much stronger than the ν_s band. The corresponding intensity transfer is not equally pronounced in the Raman spectra but the ν_{as} bands are clearly visible, especially in the perpendicularly polarised spectra because of the highly polarised nature of the symmetric ν_s mode. The frequencies are much lower than for any of the O-donors. Considering the relative intensities of the two bands, this suggests a marked deviation from XHgX linearity. The $HgCl_2$ solution in dibutylamine is more difficult to study because of severe solvent interference. A subtraction of the bands from the pure solvent spectrum displays a

TABLE I. Symmetric ν_s and Asymmetric ν_{as} Stretching XHgX Frequencies in cm^{-1} of the Neutral Mercury(II) Halide Complexes in Different Solvents at 25 °C. Frequencies from Infrared Studies are Underlined. When Available the Raman Value for ν_s and the IR Value for ν_{as} is Reported Here

	$HgCl_2$		$HgBr_2$		HgI_2		Reference
	ν_s	ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}	
Gas	358	413	221.8	293	158.4	237	43, 44
Dichloromethane	[a]	394.6	216	[a]	157	226.5	[b]
1,2-Dichloroethane	339	[a]	215	278.4	155	224.5	[b]
Benzene		391.0		278.8		[a]	[b]
	339	392	213				1
Furan	339	386	212		155	[a]	1
Nitromethane		386		276		[a]	[b]
	337		213				2
Nitrobenzene		388.5		[a]		[a]	[b]
	337		213	[a]	156		1
Triphenylphosphite			[a]		155		[b]
Methylphenylether	[a]		212		154		[b]
Acetic acid	332	380	208		[a]		1
Benzonitrile	331		210				2
Methyl acetate	332	380	210	271			2
Propylene carbonate		380		272			[b]
	330	379	210				2
Diethylether	327	380		272			[b]
	332	380	210		152		1
Tetramethylenesulfone	[a]		207		[a]		[b]
Acetonitrile	327	374.0	209.5	[a]	154	[a]	[b]
n-Butyronitrile	327		209		153		[b]
Propionitrile	327		207.5		153		[b]
Acetone	327	374.0	207	267.6	153		[b]
Diphenylsulfide	326	[a]	206	270	153	[a]	[b]
Thiophenol	[a]		[a]		152		[b]
γ-Butyrolactone	326		208		152		[b]
1,4-Dioxane	322	369	204	[a]	151	215	[b]
Tetrahydrofuran	320	370	204.5	263	151	212	[b]
Methanol	320.5	369	204	262	150	[a]	[b]
1-Butanol	321	366	203		151		1
Ethanol	321	366	202		149		1
	319		203				[b]
Tri-n-butylphosphate	318	362.5	199.5	254	147	205	[b]
Water	320	353	205	248	[a]	[a]	[b]
Formaldehyde	318		204		[a]		1
1,2-Ethanediol	317		202		151		[b]
N-Methylformamide	~318		200	~250	147.5	203	[b]
Trimethylphosphate	317		199		148	202	[b]
Triethylamine	[a]		[a]		148		[b]
Formamide	314		201		148		[b]
Tetramethylurea	313		198				2
N,*N*-Dimethylacetamide	311	356	198	249.5	146	200.5	[b]
N,*N*-Diethylacetamide	[a]		198	~246	144	198	[b]
N,*N*-Dimethylformamide	307.5	361.5	198	250.3	147	201.8	[b]
N-Methyl(2)pyrrolidone	[a]		195	244	146	198	[b]
1-Butanethiol	[a]	[a]	194.5	243	146	197	[b]
Dimethylsulfoxide	303	341.4	194	241.6	145	193.4	[b]
Tetramethylenesulfoxide	303		193	~241	144	193	[b]
Hexamethylphosphoric triamide	300		188				[b]
Aniline			188	[a]	141	[a]	[b]
	297						45
Pyridine	282	313	184	222.5	142	181	[b]
4-Methylpyridine	282		183				2

(continued)

TABLE I. *(continued)*

	$HgCl_2$		$HgBr_2$		HgI_2		Reference
	ν_s	ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}	
2-Methylpyridine	280		183				2
2,2′-Thiodiethanol	~280		183		142	~180	b
Di-n-butylsulfide	281	$\underline{303}$	181	$\underline{213}$	140	$\underline{178}$	b
Tetrahydrothiophene	278	~$\underline{288}$	179	$\underline{211}$	140.5	$\underline{177}$	b
Cyclohexylisocyanide	c	c	c	c	138		b
Tetrahydroselenophene	255	$\underline{249}$	177		135		39
Di-n-butylamine	~250	~$\underline{258}$	175	$\underline{202.5}$	137.5	$\underline{172}$	b
Piperidine	a	a	174	$\underline{190}$	135	158	b
N,N-Dimethylthioformamide	a		170		132		b
Hexamethylthiophosphoric triamide	a		169		132		b
Hexylamine			168	~$\underline{190}$	132	155	b
N-Methyl(2)thiopyrrolidone	a		166		132		b
Tri-n-butylphosphite[f]	d	d	163.5	$\underline{164}$	130.5	$\underline{136}$	b
Liquid ammonia	d	d	d	d	123		4
Tri-ethylarsine[e]	222	$\underline{211}$	150	$\underline{150}$	122	$\underline{125}$	b
Tri-n-butylphosphine	210	$\underline{200}$	146	$\underline{136}$	115.5	$\underline{113}$	b
Tri-n-butylphosphine[e]	209	$\underline{198}$	146	$\underline{134}$	122	$\underline{112}$	6
Triethylphosphine[e]	209	$\underline{195}$	146	$\underline{133}$	118	$\underline{113}$	6
Dimethylethylphosphine[e]	200	$\underline{193}$	130	$\underline{130}$	114	$\underline{112}$	6

[a] Too low solubility or solvent interference. [b] This work. [c] Reacts. [d] Dissociates. [e] In $CDCl_3$ solution. [f] Purity 80%.

broad band at about 250 cm^{-1} in the Raman and 260 cm^{-1} in the infrared spectra.

Piperidine and hexylamine solutions of $HgBr_2$ and HgI_2 show analogous results in Raman with slightly lower Hg–X frequencies. In pyridine solutions all three mercury(II) halides have been studied [11], and give somewhat higher Hg–X frequencies, Table I. Both the ν_s and ν_{as} bands are discernible in the Raman spectra of HgI_2 and $HgBr_2$, and also in the infrared spectrum of $HgBr_2$.

All the investigated amides, which have both O and N donor atoms, are found in the same frequency range as the strong O-donor solvents. Weak features in both Raman and IR spectra conflicting with the $D_{\infty h}$ selection rules can be found in most of these spectra.

The frequency lowering in the dialkyl S-donor solvents 2,2-thiodiethanol, di-n-butylsulphide and tetrahydrothiophene slightly exceeds that caused by pyridine, with two well-defined HgX_2 stretching bands in the Raman and IR spectra for the two latter solvents (except for $HgCl_2$ where the bands are broad). 1-Butanethiol, with only one butylgroup, gives a somewhat weaker effect similar to DMSO with strong ν_s and weak ν_{as} bands in the Raman spectra of the $HgBr_2$ and HgI_2 solutions. Diphenylsulphide and thiophenol interact very weakly because of the electron-withdrawing effect of the phenyl group. The thioamides all cause much stronger frequency shifts than their oxygen analogues.

Phosphorous is generally regarded as a very soft donor and phosphines are known to form a range of well-defined complexes with mercury. By far the lowest frequencies are obtained with tri-n-butylphosphine Bu_3P. Replacement of butyl by butoxy groups in tri-n-butylphosphite $(BuO)_3P$ reduces the donor properties somewhat but still gives a ligand more powerful than any of the N- or S-donors. The effect on the donor properties of phosphorous by using phenoxy groups as electron-withdrawing ligands is drastic. Mercury(II) iodide in tri-n-phenylphosphite $(PhO)_3P$ has a similar ν_s frequency to those in the non-coordinating solvents, Table I.

Solvation of $SbCl_5$

The measured ν_1(Sb–Cl) stretching frequencies for some adducts $SbCl_5 \cdot L$ in dilute 1,2-dichloroethane solutions are listed in Table II. The range of solvents studied is rather restricted for the following reasons. For a number of solvents, the alcohols, acetone and water, an excess of antimony(V) chloride was found to be necessary in order to prevent reactions other than the adduct formation taking place. For example, when acetone in excess is added to $SbCl_5$ in 1,2-dichloroethane solution, a reaction occurs which turns the mixture dark red and no Sb–Cl frequency could be found in the region 200–400 cm^{-1}. Stronger donors than pyridine reacted immediately at all concentrations. The $SbCl_5$ molecule presumably retains its trigonal bipyramidal shape from the gas phase in the non-coordinating solvents 1,2-dichloroethane and benzene. In the latter solvent there is even an upward shift of the ν_1 frequency, indicating an interaction with benzene which gives a

TABLE II. The Symmetric Stretching Frequencies ν_1(Sb–Cl) in cm^{-1} of $SbCl_5$ in Different Solvents at 25 °C. The Shifts in cm^{-1} from the Vibration Frequency in 1,2-Dichloroethane Solution, $\Delta\nu_1$, are Compared to Gutmann's Donor Numbers D_N [21]

Solvent	ν_1	$\Delta\nu_1$	D_N
$SbCl_5$(gas)[a]	355	−2	
1,2-Dichloroethane	353	0	0
Benzene	365	−12	0.1
Acetonitrile[b]	343	10	14.1
Ethanol[b]	335	18	20
Acetone[b]	334	19	17.0
Water[b]	334	19	18.0
Deuterated water[b]	333	20	
Methanol[b]	331	22	19
Diethylether[b]	330	23	19.2
$SbCl_6^-$[a]	330	23	
DMSO (O-coord.)[b]	328.5	24.5	29.8
Pyridine[b]	327	26	33.1

[a]Ref. 30. [b]In dilute 1,2-dichloroethane solution.

strengthening of the Sb–Cl bonds. In the other solvents there is a clear downward shift of the ν_1(Sb–Cl) frequency indicating an adduct formation $SbCl_5 \cdot L$. The response of ν_1 is fairly small for the coordination of solvents from ethanol to pyridine. This is probably due to the fairly hard character of the $SbCl_5$ acceptor, which tends to make the interaction largely ionic and level out the effects of the polarizability differences between the donors. The correlations with the donor numbers D_N in Table II for these solvents is, however, fairly good, and the deviations do probably not exceed the uncertainties.

Discussion

Structure of the Solvated HgX_2 Species

The structures of the neutral mercury(II) halide complexes have been determined in methanol, DMSO, pyridine and THT solutions by means of X-ray scattering and EXAFS methods [10–13]. The Hg–X bond distances increase with increasing coordinating ability of the solvent in the order methanol < DMSO < pyridine < THT, which corresponds to the decrease of the Hg–X stretching frequencies in Table I. The X–Hg–X angles also decrease in that order, Table III. Increasing solvent interaction therefore appears to go hand in hand with angular distortion.

The asymmetric stretching frequency ν_{as} decreases more rapidly than the symmetric ν_s frequency for all the three mercury(II) halides, Table I. For the most strongly coordinating solvents the ν_{as} frequency actually becomes lower than ν_s. There are some gaps in the Table, especially in the mercury(II) chloride system with very strong donors, because of dissociation or lower solubility of $HgCl_2$ in these solvents. Conductivity measurements on aqueous solutions of $[HgCl_2(PR_3)_2]$ ($PR_3 = PEt_3$ or PMe_2Et) show that the chloride complexes undergo partial ionisation [6]. In the $(BuO)_3P$ solution of $HgCl_2$ both the Raman and IR spectra display two bands in the stretching region, the stronger of which (values in parentheses in Table I) probably originates from partially dissociated species. Nevertheless, there seems to be a significant difference in the decreasing trends between the three mercury(II) halides in that the cross-over where ν_{as} equals ν_s, occurs first for the chloride and last for the iodide at increasing solvent interaction.

There are several factors that contribute to these observed effects. The first, and most important, is the decrease of the Hg–X bond strength shown by the increase in the bond length upon the solvation of the mercury atom when well-defined adducts are formed, Table III. The corresponding decrease in the stretching force constant is the main cause of the overall drop in the stretching frequencies. A secondary effect is the solvation of the bound halide atoms by hydrogen bonding, dipole–dipole or van der Waals interactions, which can cause either an upward or a downward shift in the Hg–X stretching frequencies. This contribution is minor in most cases as is shown by comparisons with measurements of the stable adducts in inert solvents (see for example the $CDCl_3$ measurements in Table I) or in solids. Also comparisons between the three mercury(II) halides in the same solvent show no significant shifts or reversals in the ranking of the donors (except possibly for water). Thirdly, the angle-dependent coupling between the symmetric and asymmetric XHgX mode, which is the main reason why they occur at different frequencies, has its maximum at an XHgX angle of 180° and decreases with decreasing angle [29]. Without any interaction with the bending mode ν_d the cross-over where ν_s equals ν_{as} would occur at 90°. In real triatomic molecules this occurs at an angle slightly over 90°, somewhat larger the heavier the ligand atoms X are [29], consistent with the trend observed here. Coupling with the donor ligands L in HgX_2L_2 can also shift the frequencies to some extent.

Attempts have been made to calculate angles on the basis of the stretching frequencies, atomic mass and stretching force-constants only; the application of this method leads to angles which are smaller than those observed by X-ray diffraction [2, 10]. Evidently the inherent approximations are somewhat too severe to be reliable. An alternative approach is to use the angles obtained from X-ray diffraction studies as a basis and relate them to the vibrational data. Some data for solid HgX_2 adducts with alkylphosphines are also included to provide a wider range, Table III. On the basic assumption that the mag-

TABLE III. Correlations Between the Frequency Shift $\Delta\nu = (\nu_{as} - \nu_s)_{gas} - (\nu_{as} - \nu_s)_{solution}$ in cm^{-1}, the Experimental XHgX Angle α and the Calculated Angle α_c in degrees from eqn. (1), and the Mean Hg–X Bond Length d in Å of the HgX$_2$ Molecules in Solution and in some Pseudotetrahedral Crystalline Compounds. The Force Constants for the Bond Stretching f_{11} and the Stretching–Stretching Interaction f_{12} from eqns. (2) and (3) are Given in N cm^{-1}. References are Given for Values Quoted from the Literature

	ν_s	ν_{as}	$\Delta\nu$	α	α_c	d	Reference	f_{11}	f_{12}	f_{12}/f_{11}
$HgCl_2$										
Gas	358	413	0	180		2.25	43, 44, 46	2.65	0.022	0.008
Benzene	339	391	3		178		1	2.38	0.021	0.009
Methanol	320.5	369	6.5	~170	174	2.308	10	2.12	0.017	0.008
DMSO	303	341.4	16.6	~165	162	2.32	10	1.86	0.050	0.027
						2.35	13			
Pyridine	282	313	24		154	2.373	11	1.58	0.050	0.032
$HgCl_2(PPh_3)_2$	237	223	69	110.7	102	2.552	6, 48	0.95	0.107	0.11
$HgCl_2(PBu_3)_2$	216	205	66	105	105	~2.61	6, 48	0.79	0.072	0.09
$HgCl_2(PEt_3)_2$	189	176	68	105.5	103	2.68	6, 48	0.59	0.066	0.11
$HgBr_2$										
Gas	221.8	293	0	180		2.41	43, 44, 47	2.28	0.033	0.015
Dichloroethane	213	278.4	5.8		180			2.08	0.053	0.025
Benzene	213	278.8	5.4		180			2.09	0.050	0.024
DMSO	195	241.6	24.6	165	158	2.455	10	1.65	0.113	0.068
Pyridine	184	222.5	32.7	151	148	2.497	11	1.43	0.092	0.064
$HgBr_2(py)_2$	182	217	36.2	141.2	144	2.480	11	1.37	0.068	0.050
THT	179	211	39.2	132	141	2.535	12	1.30	0.037	0.029
$HgBr_2(THT)_2$	168	185	54.2	117.5	124	2.553	12	1.06	0.038	0.036
$HgBr_2(PPh_3)_2$	155	164	62.2	106.9	114	2.630	6, 48	0.86	0.023	0.027
$HgBr_2(PEtMe_2)_2$	130	130	71.2	104.5	104	2.795	6, 48	0.57	0.041	0.071
HgI_2										
Gas	158.4	237	0	180		2.59	43, 44, 47	1.87	0.011	0.006
Dichloromethane	157	226.5	9.1		180			1.77	0.075	0.042
Dichloromethane	155	224.5	9.1		180			1.73	0.066	0.038
DMSO	145	193.8	29.8	159	156	2.625	10	1.39	0.123	0.089
Pyridine	142	181	39.6	143	145	2.665	11	1.24	0.096	0.077
$HgI_2(py)_2$	139	176	41.6	142.7	142	2.666	11	1.18	0.097	0.082
THT	140.5	177	42.1	143	142	2.670	12	1.20	0.107	0.089
$HgI_2(PPh_3)_2$	129	137	70.6	109.0	109	2.748	6, 49	0.82	0.062	0.076

nitude of the splitting due to the coupling between ν_s and ν_{as}, is directly related to the angle α of the XHgX entity, a correlation between the variables α and $\Delta\nu$ is sought, where the quantity $\Delta\nu$ is the difference between the splitting in the gas phase and in the solution: $\Delta\nu = (\nu_{as} - \nu_s)_{gas} - (\nu_{as} - \nu_s)_{solution}$. Figure 1 shows a plot of the available values. Considering that the number of cases in which the X-ray studies have been undertaken is rather limited and the uncertainties are fairly large, linear correlations corresponding to the lines in Fig. 1 seem to be adequate. The equations describing these lines have the form:

$$\alpha = 180^\circ - 1.16(\Delta\nu - \Delta\nu_0) \qquad (1)$$

The parameter $\Delta\nu_0$ has values of 1.5, 5.5 and 9 cm^{-1} for $HgCl_2$, $HgBr_2$ and HgI_2, respectively; it should reflect the change observed for non-coordinating solvents towards mercury(II). The inherent assumptions in these linear correlations is that the magnitude of the splitting between ν_s and ν_{as} can be represented with linear functions of the deformation angle. The variation of the bond strength and the coupling between the stretching and bending vibrations clearly makes this an approximation, but the correlations in Fig. 1 can give useful indications of the XHgX bond angle merely from vibrational data.

A consistency test on the connection between the angle α and the measured frequencies can be made by an estimation of the magnitude of the Hg–X stretching force constant f_{11} and of the stretching–stretching interaction constant f_{12}. By means of Wilson's *GF* matrix method, as applied on a bent symmetrical HgX_2 molecule in a generalized valence

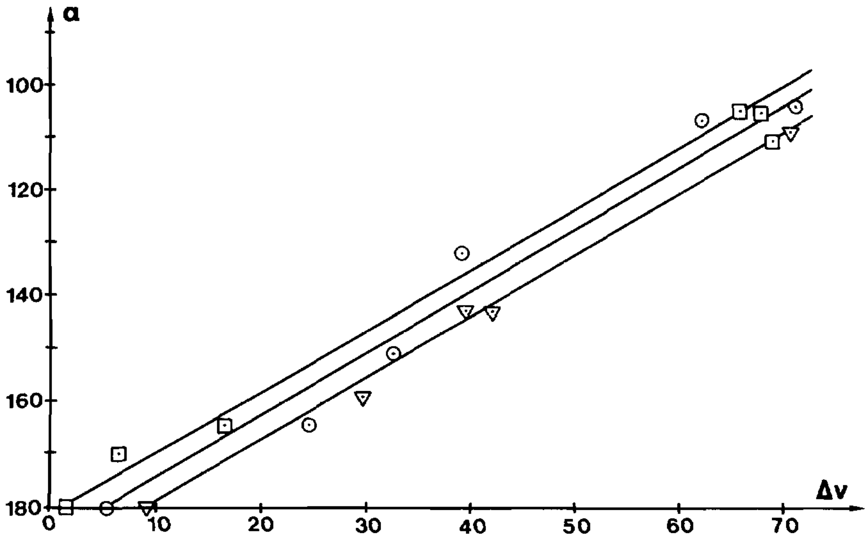

Fig. 1. The relationship between the XHgX angle α in degrees and the vibrational shift parameter $\Delta\nu$ in cm^{-1} of the mercury(II) halides with values from Table III. The symbols denote: squares $HgCl_2$, circles $HgBr_2$ and triangles HgI_2.

force field (see ref. 30, Chap. 1) the frequency ν_{as} of the B_2 mode is given by

$$4\pi c^2\nu_{as} = G_{33}F_{33}$$
$$= (f_{11} - f_{12})[m_X^{-1} + m_{Hg}^{-1}(1 - \cos\alpha)]. \quad (2)$$

The frequency ν_s belongs to the A_1 species and if all influence of interactions with the bending vibration is neglected we obtain an approximate expression for ν_s:

$$4\pi c^2\nu_s = G_{11}F_{11}$$
$$= (f_{11} + f_{12})[m_X^{-1} + m_{Hg}^{-1}(1 + \cos\alpha)]. \quad (3)$$

From these expressions the force constants f_{11} and f_{12} have been calculated (Table III) for the HgX_2 solutions and solid compounds which have been used in the construction of Fig. 1. The f_{12} values are, unlike f_{11}, very sensitive to a change in the angle α. A check on the magnitude of α is then provided by the ratio f_{12}/f_{11}. It is reasonable to expect that this ratio will be similar and change smoothly in the three HgX_2 series, as also is found with few exceptions, Table III.

The form of the interaction between mercury and the solvent varies from solely van der Waals association in the weakest cases to covalent bonding in the strongest. Since water and DMSO, weak or intermediate O-donors, are capable of inducing regular six-coordination about the Hg^{2+} ion [31], it is not clear why the solvated HgX_2 species in these solvents should not also be six-coordinate. However, available evidence from solution and solid state structures indicates enhanced and specific association to two solvent molecules on one side of the mercury atom in the HgX_2 molecules, leading to a pseudo-tetrahedral configuration. For example in DMSO solutions where the solution X-ray data were inconclusive [10], this is supported by the occurrence of the solid solvate $HgI_2 \cdot 2DMSO$ with similar Hg–I stretching frequencies in its Raman spectrum to those in solution [32].

Non-coordinating Solvents

The distinct group of solvents with almost constant stretching frequencies at the top of Table I comprises solvents not capable of interacting specifically with the mercury atom. This group also encompasses some hard oxygen donors like nitromethane, nitrobenzene and furan, which interact weakly with the soft acceptor mercury(II) and presumably solvate by van der Waals interactions. That a further frequency lowering is an indicator of a solvent association with the mercury atom is supported by a comparison of the Raman stretching frequencies of the methylmercury(II) halides in some solvents [33]. The vibration frequencies of the very stable CH_3HgX entities did only shift significantly in the strongly coordinating solvent pyridine, in which according to X-ray diffraction evidence, adduct species are formed [33].

O-Donors

For alcohols and ethers, which all contain an oxygen atom with two single bonds to protons and/or alkyl groups, there is a tendency for the symmetric stretching frequency ν_s to decrease with increasing dipole moment μ of the solvent, see Table IV. The solvating ability of methylphenylether (anisole) is, however, substantially weaker than that of dialkylethers, which is an effect of the electron-withdrawing phenyl group. Oxygen donors with a

TABLE IV. The Dipole Moment μ in *D* of some Oxygen, Nitrogen and Sulphur Donor Solvent Molecules in Gas Phase [27, 37, 50, 51] Compared to the Symmetric Stretching Frequency ν_s in cm^{-1} of HgX_2 Molecules in Solution

O-donor	μ	ν_s(Hg–Cl)	ν_s(Hg–Br)
Water	1.85	320	205
Methanol	1.70	320.5	204
Ethanol	1.69	319	203
n-Butanol	1.66	321	203
Tetrahydrofuran	1.63	323	204.5
Diethylether	1.15	332	210
N-donor	μ	ν_s(Hg–Br)	ν_s(Hg–I)
Ammonia	1.47		123
Hexylamine[a]	1.12	168	132
Piperidine	1.02	174	135
Di-n-butylamine	0.92	175	137.5
Triethylamine	0.66	199	148
S-donor	μ^b	ν_s(Hg–Br)	ν_s(Hg–I)
n-Butanethiol	1.53	194.5	146
Di-n-butylsulfide	1.80	181	140
Tetrahydrothiophene	1.90	179	140.5

[a] Extrapolated μ-value from ethylamine and n-butylamine. [b] In benzene solution.

double bond to carbon, as in organic acids, esters, ketones, aldehydes and organic carbonates, have high dipole moments but are weakly coordinating towards the mercury(II) halides. No direct correlation between the stretching frequencies and the dipole moments of these solvent could be found.

Oxygen atoms with a double bond to sulfur or phosphorous, for example in sulfoxides and trialkylphosphates, are generally the strongest oxygen donors. On coordination through the oxygen atom an increase of the ionic character of the X=O double bond occurs, and electrons can be transferred to the metal–ligand bond. This effect has been studied in detail, e.g. for DMSO [10, 30]. Such an electron redistribution does not occur to the same extent for the C=O double bond, and solvents donating through a carbonyl oxygen are consequently in general hard donors. The high donating ability of the amides towards mercury(II) is therefore presumably an effect of their ability to coordinate not only through oxygen but also through the nitrogen atom.

N-Donors

Solvents coordinating only through a nitrogen atom can be divided into three categories: nitriles, pyridines and amines. The solvating ability of the nitriles seems to be anomalously dependent on the charge of the acceptor. Acetonitrile, for example, solvates the soft univalent d^{10} ions copper(I), silver(I) and gold(I) strongly [34–36]. On the other hand, the likewise soft but divalent d^{10} mercury(II) is weakly solvated, despite the high dipole moment of acetonitrile (see Table VI). This discrimination in solvation between uni- and divalent ions seems to be a specific property of the nitriles. The other alkylnitriles studied, propionitrile and butyronitrile, are very similar to acetonitrile with only marginally stronger donor properties. Weakest of the nitrogen donors towards mercury(II) is benzonitrile, where the electron-withdrawing phenyl group further decreases the donor ability of the nitrogen atom.

Pyridine and its derivatives are regarded as soft donors and they solvate soft acceptors well [2, 33–35]. Mercury(II) is strongly solvated as shown by the ν_s values in Table I and by the structural studies [11].

The coordinating properties of alkylamines towards the soft acceptor mercury(II) in the dihalides seem to be correlated to their dipole moment, as a nearly linear relationship can be found with the ν_s-(Hg–X) frequencies (Table IV). The magnitude of the dipole moment increases for the amines in the order tertiary < secondary < primary < ammonia [37], Table IV. Triethylamine solvates mercury(II) halides poorly, but the solvating ability of liquid ammonia is so strong that only mercury(II) iodide does not dissociate completely [4]. Although less powerful than the primary alkylamines aniline is still a strong donor despite the electron-withdrawing phenyl group.

S-Donors

An alkylsubstitution of a hydrogen atom of H_2S increases the dipole moment contrary to the effect on NH_3, Table IV. Nevertheless, the same tendency of the ν_s(Hg–X) frequency to decrease with increasing dipole moment remains. For all the solvent pairs studied where an oxygen atom has been replaced by a sulfur atom, *i.e.* tetrahydrofurane–tetrahydrothiophene, 1-butanol–1-butanethiol, hexamethylphosphoric triamide–hexamethylthiophosphoric triamide, *N*-methyl(2)pyrrolidone–*N*-methyl(2)-thiopyrrolidone, and *N,N*-dimethylformamide–*N,N*-dimethylthioformamide, the softer thiocompound has a considerably stronger donating ability towards mercury(II), Table I. Again the phenyl group decreases the donating ability substantially, as the comparisons between butanethiol and thiophenol, or di-n-butylsulfide and diphenylsulfide show.

Se-Donors

A pseudo-tetrahedral coordination of two tetrahydroselenophene, SeC_4H_8(THSe), molecules has recently been found in the crystal structures of $HgI_2(SeC_4H_8)_2$ and $HgBr_2(SeC_4H_8)_2$ [38]. The molecular structure is very similar to that found for the corresponding cyclic sulphur ligand tetrahydrothiophene SC_4H_8(THT) in the compounds $HgBr_2(THT)_2$ and $HgCl_2(THT)_2$ [12], Table III, with longer Hg–Br bonds (average value 2.603 Å) and a slightly smaller

BrHgBr angle (110.1°) in the $HgBr_2(THSe)_2$ compound. The vibrational spectra of HgX_2 (X = Cl, Br and I) in THSe solutions were also recorded [39], and gave slightly lower frequencies than the corresponding THT solutions, Table I. The largest difference was observed for the $HgCl_2$ solutions, which gave broad and weak bands in both solvents. This may also be connected with an even lower stability of the solvated $HgCl_2$ complex in THSe, indicated by the non-successful attempt to prepare a solid $HgCl_2(THSe)_2$ compound [39].

In accordance with the previous classifications already made the solution vibrational data show the Se-atom to be a marginally stronger donor than the S-atom towards a soft acceptor, for these directly comparable ligands. The same conclusion can also be drawn from a comparison of the structural data mentioned above.

P-Donors

The solubility of the mercury(II) halides in phosphines is generally low in spite of the extreme solvation. The stable $HgX_2(PR_3)_2$ complexes have, however, been studied in $CDCl_3$ solution [6]. All of the phosphines including triphenylphosphine, solvate soft acceptors more strongly than any of the other solvents, except liquid ammonia, Table I. For solubility reasons and to avoid dissociation of the mercury(II) halide molecules in these solvents, some measurements of the phosphine adducts in deuterated chloroform ($CDCl_3$) solution [6] have been included in Table I. For tri-n-butylphosphine measurements have also been made in the neat solvent, with frequencies not very different from those obtained in $CDCl_3$ solution. We therefore feel that the $CDCl_3$ values can be used for qualitative comparisons.

As-Donors

A measurement of $HgX_2(AsEt_3)_2$ adducts in $CDCl_3$ solution has been made, Table I. Although the values may be slightly shifted compared to values from the undiluted solvent, it is clear that the strongly coordinating triethylarsine is intermediate between triethylamine and triethylphosphine in its coordinating properties towards mercury(II).

C-Donors

Cyclohexylisocyanide (isocyanocyclohexane) coordinates strongly to mercury(II) halide through its carbon atom but reacts also fairly rapidly with the mercury(II) halides and is not suitable as a solvent [40]. Carbon is generally a very soft electron pair donor and forms, especially in carbanions very strong bonds to mercury(II), as for example in alkylmercury(II) halides and dialkylmercury(II).

Ranking of Donors

Several attempts have been made to correlate the ν_s(Hg–X) frequencies with physical properties of the solvent [1, 2]. Dielectric constants, Gutmann's donor numbers, Koppel and Paju's basicity parameters, Dimroth–Reichardt acidity parameter E_T, and acid dissociation constants in water have been tried with rather poor success [2]. However, Table IV shows that correlations with the dipole moment can be found within very restricted sets of solvents. For solvents with the same type of donor atom in structurally closely related compounds, for example when protons are replaced with alkyl groups, the shift $\Delta\nu_s$ seems to be related to the dipole moment. On the other hand, when electron-withdrawing conjugated systems like phenyl groups are attached to the donor atom, its donor ability decreases considerably in all cases. These are observations in line with those of Taft *et al.* [41] who found that for non-protonic aliphatic solvents with a single dominant bond dipole (*i.e.* solvents wherein hydrogen bonding is excluded and polarizability effects are similar), the various solvent property scales are linear with one another and with the solvent molecular dipole moment μ.

It is of interest to note that we find such an energy response towards the dipole moment under similar conditions also for adducts with mercury(II) halides for which a significant amount of covalent bonding can be expected. This is in line with the view that 'the permanent electrostatic and the covalent terms in the chemical bonds both are basically of electrostatical nature' [14]. The distinction often implied between electrostatic and covalent bonds originates from the classical division of the interaction into an electrostatic effect from permanent or induced charge separations, and a covalent term which can be related to the redistribution of the valence electrons in the adduct system. The effective electric dipole moment of a coordinated solvent molecule is also a complex quantity, composed of a permanent component μ and an additional contribution μ_{ind} induced by the polarization of the molecular orbitals in the electrical field from the acceptor atom [37]. It is therefore necessary that both the donor–acceptor atom distances and the polarizabilities of the solvent molecules are similar, in the order to find linear relationships between the adduct bond strength and the experimental permanent μ value for a set of solvents. For non-linear relations quantum-mechanical *ab-initio* calculations of the polarization contribution μ_{ind} which is expected to be quite large in soft–soft interactions would be necessary in order to predict and understand the effects.

A Donor Scale for a Soft Acceptor

Although a number of scales ranking donor properties of solvents has been proposed, there is a clear need of a scale for soft acceptor atoms. The shift of the symmetric stretching frequency from gas phase to solution of the $HgBr_2$ molecule has therefore been used to construct a scale, D_S. The donor strength of a solvent molecule will for a soft acceptor atom such as Hg depend strongly on the polarizability of the donor atom. The proposed donor strength scale should therefore be valid mainly for acceptors of similar softness as Hg in the $HgBr_2$ entity. An indication that the applicability is not too restricted is the close response of vibrational frequencies for the three halides HgX_2 (X = Cl, Br or I), Table I.

The reasons for and the assumptions inherent in the proposed D_S scale are the following:

— Adducts of a defined composition $HgBr_2L_2$ seem to be formed in almost all cases of medium to strong interaction in solution (and often in solids), and for weakly coordinating solvents there is a strong correlation between the frequency response and some other measures of the solvent donor strength, Table V and Fig. 2.

— The vibrational shift is a molecular property directly related to the Hg–L bond strength, although not necessarily as a linear function.

— The scale is obtained for an atom with soft character, which makes it complementary to other scales based on hard or borderline acceptors.

— The $HgBr_2$ complex is a stable entity, which in combination with its softness allows a large range of very strongly donating solvents to be studied.

— Measurements are quick and easy to perform with access to a Raman spectrometer, and the solubility of $HgBr_2$ is sufficient in most solvents to allow a precision better than 1 cm^{-1} (*i.e.* 1 unit on the D_S scale).

— The bromide atoms of the $HgBr_2$ entity have little tendency to participate in hydrogen bonding. The ability of solvents to form hydrogen bonds will therefore not influence the measured donor ability to any great extent, although electrostatic interactions with solvent dipoles and the resident charge on the Br atoms could indirectly affect the Hg–solvent bond strength.

— The measurements are normally performed in the undiluted solvent, which means that the effect on the Hg–L bonds by solvent–solvent interactions between the coordinated and the bulk solvent is accounted for. This seems to be especially important for some of the sulfur-donor solvents, where anomalous enthalpy effects have been found [23].

— Steric effects are not expected to be important as there is little crowding of the four ligands in a pseudo-tetrahedral $HgBr_2L_2$ configuration.

— The $HgBr_2$ molecule is preferable to its $HgCl_2$ or HgI_2 analogues for the following reasons: it has a high solubility in a wider range of solvents, less interference with solvent vibrational or Rayleigh bands in the Raman spectra, higher stability and smaller tendency to hydrogen-bond formation than $HgCl_2$ and better frequency-response than HgI_2 upon solvation.

Comparisons of the D_S donor strength values with some other donor scales are made in Table V. Because they refer to acceptors with harder properties than

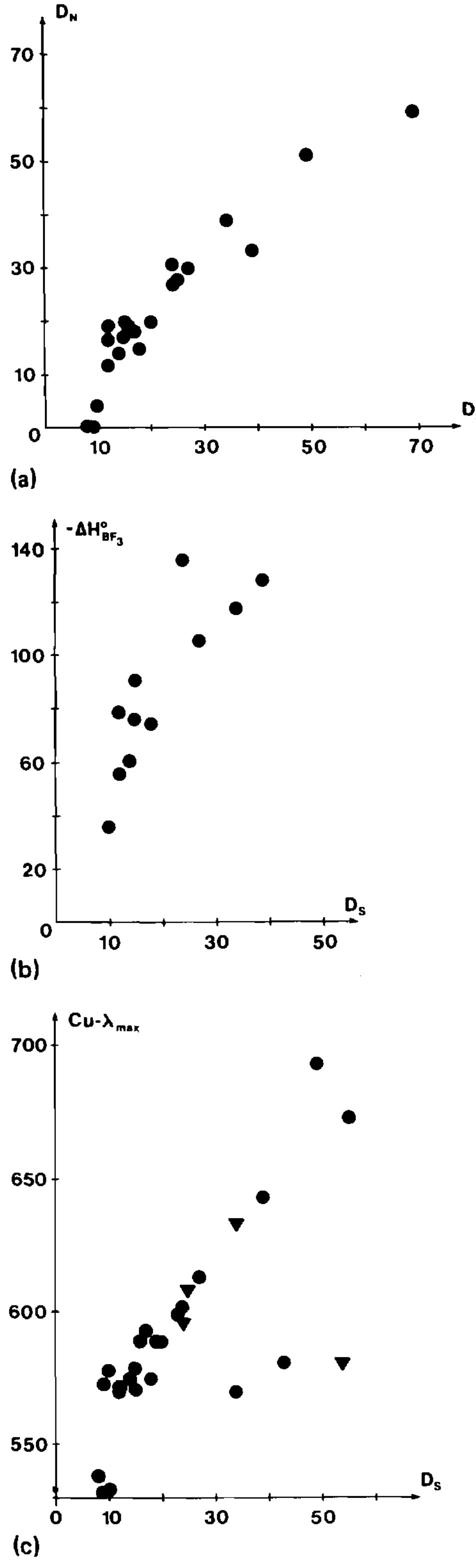

Fig. 2. Correlations between different scales of solvent donor properties. (a) The donor numbers D_N, (b) the $\Delta H^\circ(BF_3)$ values, and (c) the Cu–λ_{max} values, are plotted against the donor strength D_S values for the solvents in Table V, the triangles denote data from ref. 42 in Table V.

TABLE V. A Comparison Between Different Scales of Donor Properties. The Donor Strength Scale D_S is Compared to Gutmann's Donor Numbers D_N [21], the $\Delta H°(BF_3)$ Values of Maria and Gal [16], and the Cu–λ_{max} Scale [26]

Solvent	D_S	D_N	$-\Delta H°(BF_3)$	Cu–λ_{max}
Dichloromethane	6		10.0	550
1,2-Dichloroethane	7	0^{a}		538
Benzene	9	0.1		
Nitromethane	9	2.7	37.6	532^{b}
Nitrobenzene	9	4.4	35.8	533^{b}
Furan	10	4.3		578
Triphenylphosphite	10^{c}			
Methylphenylether	10	7.9		573
Benzonitrile	12	11.9	55.4	572
Propylene carbonate	12	15.1	64.2	554^{b}
Methylacetate	12	16.5	72.8	570
Diethylether	12	19.2	78.8	
Acetonitrile	12	14.1	60.4	575
Thiophenol	13^{c}			
n-Butyronitrile	13	16.6	61.2	
Propionitrile	14	16.1	61.0	
Acetic acid	14	10.5		
Butyrolactone	14			568
Tetramethylenesulphone	15	14.8	51.3	562
Acetone	15	17.0	76.0	571^{b}
Diphenylsulphide	16			
Tetrahydrofuran	17	20.0	90.4	579^{b}
Water	17	18.0		591
Methanol	18	19		589
Formaldehyde	18			
Dioxane	18	14.8	74.1	575
n-Butanol	19	24.0		589
Ethanol	19	20		589
1,2-Ethanediol	20			579
Formamide	21	24		598^{b}
N-Methylformamide	22			604
Tri-n-butylphosphate	22	23.7		599
Trimethylphosphate	23		84.8	596
Triethylamine	23^{c}	31.7^{d}	135.9	
Tetramethylurea	24	31	108.6	596^{e}
N,*N*-Diethylacetamide	24	32.2	113.6	
N,*N*-Dimethylformamide	24	26.6	110.5	603^{b}
N,*N*-Dimethylacetamide	24	27.8	112.1	608
N-Methyl(2)pyrrolidone	27		112.6	
1-Butanethiol	27			
Dimethylsulfoxide	28	29.8	105.3	608^{e}
Tetramethylenesulfoxide	29			613
Hexamethylphosphorictriamide	34	38.8	117.5	633^{e}
Aniline	34	33.3		570
Pyridine	38	33.1	128.1	638^{b}
2-Methylpyridine	39		123.4	
4-Methylpyridine	39		134.2	
2,2′-Thiodiethanol	39			
Di-n-butylsulfide	41			
Tetrahydrothiophene	43		51.6^{f}	606
Tetrahydroselenophene	45^{g}			
Cyclohexylisocyanide	45^{c}			
Di-n-butylamine	47			
Piperidine	48	51		695^{b}
N,*N*-Dimethylthioformamide	52			413^{e}
Hexamethylthiophosphoric triamide	53			581
Hexylamine	54	57		673

(continued)

TABLE V. *(continued)*

Solvent	D_S	D_N	$-\Delta H°(BF_3)$	Cu–λ_{max}
N-Methyl(2)thiopyrrolidone	56			763[e]
Tri-n-butylphosphite	58			
Liquid ammonia	69[c]	59		
Triethylarsine	72			
Tri-n-butylphosphine	76			
Triethylphosphine	76			
Dimethylethylphosphine	92			

[a]By definition. [b]Ref. 25. [c]Estimated from ν_s(Hg–I). [d]Ref. 22. [e]Ref. 42. [f]Ref. 52. [g]Ref. 39.

TABLE VI. A Comparison Between the D_H Scale for Hard Acceptors and the D_N and D_S Scales. The Free Energies of Transfer $\Delta G°_{tr}$ of Na$^+$ from Water to Other Solvents in kJ mol^{-1} [34, 35], which are Used to Derive the D_H Values, and the Dipole Moment μ in D at 25 °C of the Solvent Molecules in Gaseous Phase [27, 37, 50, 51] are Included

Solvent	$\Delta G°_{tr}$	D_H	D_N	D_S	μ
N,*N*-Dimethylthioformamide	39	−14		52	
Nitrobenzene	34	−9	4.4	9	4.22
Tetrahydrothiophene	29.1	−4.4		43	1.90[c]
1,1-Dichloroethane	29	−4			2.06
Nitromethane	(26)	(−1)	2.7	9	3.46
Benzonitrile	24.8	−0.1	11.9	12	4.18
1,2-Dichloroethane	24.7	0[a]	0[a]	7	1.75[c]
Propanol	16.8	7.9		19[b]	1.68
Pyridine	16.0	8.7	33.1	38	2.19
Acetonitrile	14.8	9.9	14.1	12	3.92
Propylene carbonate	14.6	10.1	15.1	12	4.98
1-Butanol	13.7	11.0	24.0	19	1.66
Methylacetate	11.4	13.3	16.5	12	1.72
Ethanol	11	14	20	19	1.69
Methanol	8.0	16.7	19	18	1.70
Acetone	4.0	20.7	17.0	15	2.88
Water	0[a]	24.7	18.0	17	1.85
Tetramethylenesulfone	−3	28	14.8	15	4.71[c]
Formamide	−8	33	24	21	3.73
Tetrahydrofuran	−9	34	20.0	17	1.63
N,*N*-Dimethylformamide	−9.6	34.3	26.6	24	3.82
N,*N*-Dimethylacetamide	−12.1	36.8	27.8	24	3.81
Dimethylsulfoxide	−13.1	37.8	29.8	28	3.96
Liquid ammonia	−13	38	59	69	1.47
N-Methyl(2)pyrrolidone	−15	40		56	

[a]By definition. [b]Estimated value. [c]In benzene solution.

the D_S scale the best correlation is obtained for weakly interacting donors. It is also evident that the range of 'non-coordinating' solvents is smaller the harder the acceptor is. The ranking of the solvents is nevertheless similar for the D_S scale, Gutmann's donor numbers D_N and the ΔH_{BF_3} scale. The comparison also support Schmid's suggestion (see Table I in ref. 28) that the 'bulk donicity' corrections for the donor numbers in the highly structured neat solvents water, methanol and ethanol, would increase the D_N values in the Table by a few units only.

The best correlation with the D_S values is, however, obtained using the solvent basicity scale Cu–λ_{max} [26] for the borderline acceptor [Cu(tmen)(acac)]$^+$. The original values have been extended to encompass 38 solvents [34, 42]. Figure 2c shows the values obtained for THT, hexamethylthiophosphoric triamide and aniline to be out of line, while for *N*,*N*-dimethylthioformamide and *N*-methyl(2)thiopyrrolidone they even fall outside the boundaries of the Figure. Phosphines reduce Cu(II) in the complex to Cu(I), and it seems likely that a reaction can occur also with these sulphur donor solvents. If the above mentioned solvents are excluded, a correlation coefficient $r = 0.95$ is obtained for the remaining 33 solvents, Fig. 2c.

A Hard Acceptor Scale

The sodium ion is regarded as a typical hard acceptor [14], which means that the electrostatic terms are expected to dominate the Na^+–solvent interactions. The Gibbs free energy of transfer (ΔG°_{tr}) of Na^+ from the solvent studied to a reference solvent, is a relative measure of the energy of solvation and of the restructuring of the solvent, and can be utilized in an attempt to rank the donor strength of solvents towards a hard acceptor. The D_H concept, the donor strength relative to a hard acceptor, with the same reference solvent as in the donor number (D_N) scale, 1,2-dichloroethane, is therefore introduced. The numerical D_H values, *i.e.* the $\Delta G^\circ_{tr}(Na^+)$ in kJ mol^{-1} to 1,2-dichloroethane, have been obtained from literature data of $\Delta G^\circ_{tr}(Na^+)$ from water [35, 36], and are compared in Table VI with the D_N and D_S scales, and with the solvent molecular dipole moment μ. Not surprisingly there is an almost random correlation between the D_H values and the D_S and D_N scales. The largest differences are found on the one hand for the soft S and N donors which give high D_S values, and on the other for the hardest O-donor solvents, which solvate the sodium ion particularly well. The electric dipole moment of the solvent molecules might be expected to correlate better with the D_H values than with D_S (Fig. 3). It is, however, evident that only closely related solvents such as the alcohols show the expected increase of the D_H values with increasing μ values. The differences in the ion–dipole distances and in the induced polarization of the solvent molecules are clearly factors that have to be accounted for. In particular nitrobenzene and nitromethane have low D_H values in spite of their high dipole moments. The low D_H values of the sulfur donor solvents *N,N*-dimethylthioformamide and THT are notable. They probably reflect not only weak donor properties towards Na^+, but also a possible breakdown of specific sulfur–sulfur–solvent interactions, an observation consistent with other results [23, 53]. The anomalously low value of $-\Delta H^\circ$ (BF_3) for THT (Table V) indicates similar effects also with the use of the acceptor BF_3.

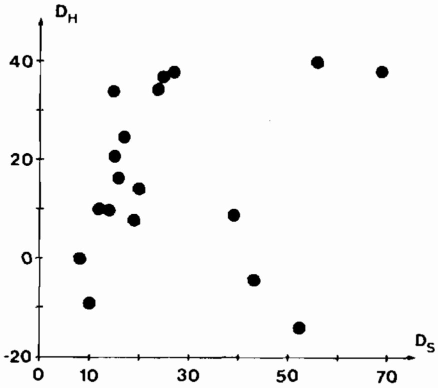

Fig. 3. The donor scale D_H (for a hard acceptor) is plotted against the D_S scale (for a soft acceptor) for the solvents in common gives an almost random correlation.

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References

1 J. H. Smith and T. B. Brill, *Inorg. Chim. Acta, 18,* 225 (1976).
2 D. N: Waters and Z. Kantarci, *J. Raman Spectrosc., 6,* 251 (1977).
3 K. Sone, M. Aritaki, K. Hiraoka and Y. Fukuda, *Bull. Chem. Soc. Jpn., 49,* 2015 (1976).
4 D. J. Gardiner, A. H. Haji and B. Straughan, *J. Chem. Soc., Dalton Trans.,* 705 (1981).
5 S. Ahrland, L. Kullberg and R. Portanova, *Acta Chem. Scand., Ser. A, 32,* 251 (1978).
6 N. A. Bell, T. D. Dee, P. L. Goggin, M. Goldstein, R. J. Goodfellow, T. Jones, K. Kessler, D. M. McEwan and I. A. Nowell, *J. Chem. Res. (S),* 2 (1981); *J. Chem. Res. (M),* 201 (1981).
7 Y. Farhangi and D. P. Graddon, *Aust. J. Chem., 29,* 983 (1973).
8 M. J. Gallagher, D. P. Graddon and A. R. Sheikh, *Aust. J. Chem., 29,* 759, 2409 (1976).
9 T. R. Griffiths and R. A. Anderson, *J. Chem. Soc., Faraday Trans. II, 75,* 957 (1979).
10 M. Sandström, *Acta Chem. Scand., Ser. A, 32,* 627 (1978).
11 I. Persson, M. Sandström, P. L. Goggin and A. Mosset, *J. Chem. Soc., Dalton Trans.,* 1597 (1985), and refs. therein.
12 M. Sandström and I. Persson, *J. Chem. Soc., Dalton Trans.,* in press.
13 J. E. Penner-Hahn, I. Persson and K. O. Hodgson, to be published.
14 W. B. Jensen, *Chem. Rev., 78,* 1 (1978), and refs. therein.
15 T. R. Griffiths and D. C. Pugh, *Coord. Chem. Rev., 29,* 129 (1979), and refs. therein.
16 P.-C. Maria and J.-F. Gal, *J. Phys. Chem., 89,* 1296 (1985).
17 R. S. Drago, *Coord. Chem. Rev., 33,* 251 (1967).
18 V. Gutmann and E. Wychera, *Inorg. Nucl. Chem. Lett., 2,* 257 (1966).
19 V. Gutmann, A. Steininger and E. Wychera, *Monatsh. Chem., 97,* 460 (1966).
20 U. Meyer and V. Gutmann, *Struct. Bonding (Berlin), 12,* 113 (1972).
21 V. Gutmann, 'The Donor Acceptor Approach to Molecular Interactions', Plenum, New York/London, 1978, Chap. 2.
22 R. W. Taft, N. J. Pienta, M. J. Kamlet and E. M. Arnett, *J. Org. Chem., 46,* 661 (1981).
23 I. Persson, M. Landgren and A. Marton, *Inorg. Chim. Acta, 116,* 135 (1986).
24 S. Hahn, W. M. Miller, R. N. Lichtenthaler and J. M. Prautsnitz, *J. Solution Chem., 14,* 129 (1985).
25 K. Sone and Y. Fukuda, 'Studies in Physical and Theoretical Chemistry', Vol. 27, Elsevier, Amsterdam, 1982.
26 R. W. Soukup and R. Schmid, *J. Chem. Educ., 62,* 459 (1985).
27 J. A. Riddick and W. B. Bunger, 'Techniques of Chemistry', Vol. II, 'Organic Solvents', Wiley-Interscience, New York, 1970.

28 R. Schmid, *J. Solution Chem.*, *12*, 135 (1983).

29 J. Weidlein, U. Müller and K. Dehnicke, 'Schwingungsspektroskopie', Georg Thieme Verlag, Stuttgart/New York, 1982, Chap. 5.3.

30 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 3rd edn., Wiley, New York, 1978.

31 M. Sandström, I. Persson and S. Ahrland, *Acta Chem. Scand., Ser. A*, *32*, 607 (1978).

32 J. P. Joly and I. F. Nicolau, *Spectrochim. Acta, Part A*, *35*, 281 (1979).

33 A. Iverfeldt and I. Persson, *Inorg. Chim. Acta*, *111*, 171 (1986).

34 I. Persson, *Pure Appl. Chem.*, *58*, 1153 (1986).

35 M. Johnsson and I. Persson, *Inorg. Chim. Acta*, *127*, 15 (1987).

36 Y. Marcus, *Pure Appl. Chem.*, *55*, 977 (1983).

37 P. M. Kuznesov, F. B. T. Pessine, R. E. Bruns and D. F. Shriver, *Inorg. Chim. Acta*, *14*, 271 (1975).

38 C. Stålhandske and F. Zintl, *Acta Crystallogr.*, (1987) in press.

39 F. Zintl, *Thesis*, 1986, Inorganic Chemistry 1, Chemical Center, University of Lund, Sweden.

40 H. Sawai and T. Takizawa, *Bull. Chem. Soc. Jpn.*, *49*, 1906 (1976).

41 J.-L. M. Abboud, R. W. Taft and M. J. Kamlet, *J. Chem. Res. (S)*, 98 (1984).

42 G. Gritzner, personal communication, Johannes Kepler Universität Linz, A-4040 Linz-Auhof, Austria.

43 R. H. J. Clark and D. M. Rippon, *J. Chem. Soc., Faraday Trans. II*, *69* 1496 (1973).

44 W. Klemperer and L. Lindeman, *J. Chem. Phys.*,*.25*, 397, 1066 (1956).

45 I. S. Ahuja and R. Rastogi, *J. Inorg. Nucl. Chem.*, *32*, 2085 (1970).

46 K. Kashiwabara, S. Konaka and M. Kimura, *Bull. Chem. Soc. Jpn.*, *46*, 410 (1973).

47 P. A. Akishin, V. P. Spiridonov and A. N. Kodchenkov, *Zh. Fiz. Khim.*, *33*, 20 (1959).

48 N. A. Bell, T. D. Dee, M. Goldstein, P. J. McKenna and I. W. Nowell, *Inorg. Chim. Acta*, *71*, 135 (1983).

49 L. Fäldt, *Chem. Scr.*, *9*, 71 (1976).

50 'Handbook of Chemistry and Physics', 65th edn., CRC Press, West Palm Beach, 1984–85.

51 A. L. McClellan, 'Table of Experimental Dipole Moments', Vol. 2, Rohara Enterprises, El Cerrito, 1974.

52 P.-C. Maria and J.-F. Gal, personal communication, Université de Nice, F-06034, Nice, France.

53 M. Johnsson and I. Persson, *Inorg. Chim. Acta*, (1987) in press.