HYDROGEN AND COORDINATION BONDS IN ISOSTRUCTURAL SYSTEMS. ARE HYDROGEN BONDS UNIQUE?

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ABSTRACT

Reliable spectral criteria which allow comparison of the hydrogen and coordination bonds in isostructural systems are suggested. The model systems consist of ArXH and ArXMR$_n$ (X = O, S, N; M = Hg, Sn, Pb, Sb; Ar = C$_6$H$_4$Y where Y = COR, NO$_2$, C$_5$H$_4$N, etc.) which interact with various N-, P- and O-bases. The conditions on which the ν_{XM} vibrations are local, have been established. Examination of thiol derivatives reveals the similarity of spectral (IR, Raman) effects for coordination and hydrogen bonds in the ν_{XM} and ν_{XH} regions, respectively. The character of dependence of a proton and a bulky organometallic cation transfer on medium, a heteroatom X or a base is shown to be similar. Some quantitative and qualitative relationships between XH and XM bond polarities and the capacity to form complexes, ionic pairs or ions are found. Comparison of spectral properties of isostructural systems with hydrogen and coordination bonds does not reveal the uniqueness of the H bond.

INTRODUCTION

Univalent organometallic R$_n$M type groups including a heavy non-transition metal (Hg, Sn, Pb, Sb, Bi) may be regarded as structural fragments of the corresponding organometallic derivatives of HX acids. The properties of these organometallic groups are very similar to those of a hydrogen atom in HX acids owing to a whole complex of common properties. In the first place, along with univalence, one should note an ability to form localized two-electron two-centre covalent σ-bonds. In accordance with the electronegativity of the "clue" atoms, metal–element σ-bonds formed by the R$_n$M groups are expected to have a minimal polarity for bonds formed by non-transition metals, with a value close to the polarity of analogous hydrogen–element bonds. Another point of similarity is the ability to act, under certain conditions, as acceptors of a lone electron pair or π-electron density to form intra- and intermolecular coordination and hydrogen bonds [1–3]. The next notable common feature is a high migratory ability which the coordinated groups and a hydrogen atom exhibit when at-

tached to a heteroatom. This ability manifests itself in rapid prototropic [4], σ-metallotropic processes [5], and exchange reactions [3, 6].

These factors encouraged us to carry out a comparitive spectral study of hydrogen and coordination bonds in isostructural systems. The systems studied consisted of compound with XH and X–M bonds interacting with the same bases under identical conditions (solvent, temperature). Their organic moieties are structurally analogous. Such an approach is of considerable interest not only for finding general relations between a structure, coordination ability and the properties of organic and organometallic compounds in various media; since this approach enables one to determine features common to hydrogen and coordination bonds, it might also provide valuable insight into the nature of different types of intermolecular interactions and elucidate the uniqueness of the hydrogen bond.

A hydrogen bond is usually compared with lithium bonding or the bond in donor–acceptor complexes [7, 8]. From such a comparison, uniqueness stems from the substantial polarity of the bonds formed by lithium and from differences in the energy of hydrogen bonds and stable complexes. According to Umeyama and Morokuma [7], the uniqueness of "normal" (i.e. moderate force) hydrogen bonding lies in the basic fact that it always involves a moderately polar, short and strong HX bond as the proton donor (electron acceptor). For these reasons, a hydrogen bond is rather weak and has a directional character. As the X-ray data show [9], the coordination bonds of a $XM \cdots B$ type also have a directional character. Taking into account the data on complexes with stronger Lewis acids [10], one may assume that the stabilities of these bonds do not exceed those of hydrogen bonds. The XM bonds, acting as electron acceptors, are very close to XH in terms of polarity, as already noted. These facts provide a good basis for comparison. On the other hand, the greater size and polarizability of organometallic groups, and the lower stabilities of XM bonds when compared with those of XH, comprise the specificity which could reveal the unique features of the hydrogen bond and its spectral manifestations.

XH acids of type ArXH and their organometallic derivatives $ArXMR_n$ ($M = Hg$, Sn, Pb, Sb) have been chosen as appropriate model systems. These can be conveniently modified on replacement of a heteroatom ($X = O$, S, N) and by introducting different substituents ($Ar = C_6H_4Y$, where $Y = COR$, NO_2; C_5H_4N, etc.), thus making it possible to vary widely the properties of XH and XM bonds. These compounds are suitable for studying with electron and vibrational spectroscopy.

First, reliable spectral criteria for formation of coordination bonds of the $XM \cdots B$ type and for a MR_n cation transfer are required.

THE ν_{XM} AND ν_{XH} VIBRATIONS, THE PROBLEMS OF COORDINATION

The vibrations ν_{XH}, which have long been extensively used in hydrogen-bond studies, are well localized, the potential energy distribution (PED) ex-

ceeding 99%. The ν_{XM} vibrations may find a use in coordination-bond study only on condition that these vibrations are characteristic for the given bond. The series of approximate normal coordinate analyses has shown that the contribution of XM bond stretching to PED is greater than 70–80% provided the masses of atoms X and M are greater than or equal to 30. Hence, the stretching vibrations ν_{XM} may be used to examine self-association, hetero-association and intramolecular coordination in the case of compounds with a heavy heteroatom–heavy metal bond[11]. The heavy metals Hg, Sn, Pb and Sb and heavy heteroatom sulphur, for example meet these requirements.

To investigate the nature of coordination bonds, a large number of organometallic derivatives of aromatic and aliphatic thiols ($R'SMR_n$) were examined in the low-frequency region. As a preliminary, the assignment of the infrared bands and the lines in the Raman spectra is proposed.

The results obtained lead to the conclusion that self-association and coordination of the studied compounds with the solvent (pyridine) display almost the same spectral effects as the vibrations ν_{XH} do upon hydrogen-bond formation. Namely, when the coordination bonds are formed, the bands ν_{XM}, assigned to vibrations of the bonded groups, shift towards lower frequencies and increase in width substantially (some examples are presented in Table 1). The magnitudes of these effects are determined by coordination bond stabilities

TABLE 1

The ν_{SM} vibrations and $\Delta\nu_{1/2}$ (cm^{-1}) in the spectra of the compounds RSMPh$_n$

RSMPh	Solid state		C_6H_6				Pyridine
	Raman ν	IR ν	Raman ν	$\Delta\nu_{1/2}$	IR ν	$\Delta\nu_{1/2}$	Raman ν
PhHgSC$_2$H$_5$	335 (1.5)[a]	336 (s,br)	320 (2.5)	32	323		320
			370 (1.3)	20	369	20	370
PhHgS(CH$_2$)$_3$CH$_3$	345 (4.5)	340 (br)	348	42	350 (br)	44	350
	370 (sh)	370 (sh)	370 (sh)		370 (sh)		370 (sh)
PhHgSPh	365 (2.5)	365 (m)	370 (br)	48	370	45	
	380 (sh)	376 (w)					
PhHgSC$_6$H$_4$(2,6-CH$_3$)	340 (2)	340 (m)					
	365 (3)	365 (m)	363	20	363	15	356
PhHgSC$_5$H$_4$N-4	240		330				330
Ph$_3$PbSC$_5$H$_4$N-4	260		320				
PhHgSC$_6$H$_3$N(CH$_3$)$_2$-4	383 (4.5)						380
PhHgSC$_6$H$_3$N(CH$_3$)-2	354 (1.5)				355		355
Ph$_3$SnSC$_6$H$_3$N(CH$_3$)$_2$-4	385 (3.1)	384	383		383		381
Ph$_3$SnSC$_6$H$_3$N(CH$_3$)$_2$-2	355 (3)	355	355		354		354

[a]Relative intensities in parentheses ($I\nu_{SM}/I_{990}$ cm^{-1}, I_{990} $cm^{-1}=10$).
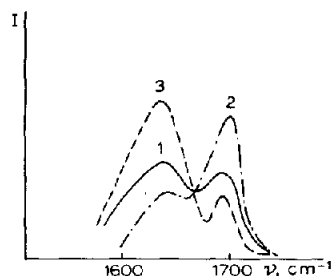
Fig. 1. Concentration and temperature dependence of the ν_{CO} vibrations for $Ph_3SnOC_6H_4COOCH_3$. (1) $c=0.2$ mol l^{-1}, $T=25\,°C$. (2) $c=0.02$ mol l^{-1}, $T=25\,°C$. (3) $c=0.02$ mol l^{-1}, $T=-70\,°C$.

[11, 12]. This was proved examining self-association of the compounds which characterized with X-ray data [9]. In the case of weak coordination, when the S–M bond distance undergoes almost no change, and the intermolecular distance S$\cdots$M is shorter by 0.1 Å than the sum of van der Waals' radii, the changes of ν_{SM} are small, i.e. $\Delta\nu \leq 20$–30 cm^{-1} ($\Delta\nu_{SM}/\nu_{SM} \leq 10\%$). Such changes were observed for PhSHgPh and PhHgSAlk type compounds in proceeding from solid state to solution. For solutions, concentration dependence is clearly indicated, and the band widths of the bonded groups are 2–3 times as great as those of the free ones (Fig. 1). In the case of strong coordination, when S–M bond distances are elongated by 0.1 Å and intermolecular distance is reduced by 0.6 Å compared with the sum of van der Waals radii [9], spectral changes become more pronounced. For instance, in systems of the type $NC_5H_4SMR_n \cdots NC_5H_4SMR_n$ the values of $\Delta\nu$ are 60–100 cm^{-1} ($\Delta\nu/\nu > 20\%$).

On cyclic chelate formation no difference can be seen between frequencies ν_{SM} in the solid state and in solvents of various polarities (C_6H_6, CH_2Cl_2, Py); there is also no concentration dependence (Table 1). The formation of five-membered cycles, e.g. in organometallic derivatives of 2-dimethylaminothiophenol, leads to a small low-frequency shift (5–30 cm^{-1}) compared with ν_{SM} for analogous compounds with no intramolecular coordination bonds, i.e. the derivatives of 4-dimethylaminothiophenol. In other words, the changes are similar to those arising from intramolecular hydrogen bonding in the ν_{XH} region.

Thus, we have demonstrated the similarity of the spectral effects of coordination and hydrogen bonds in the ν_{SM} and ν_{XH} regions, respectively, which are revealed under self-association, hetero-association and intramolecular coordination.

VIBRATIONS OF THE SUBSTITUENTS (ν_{CO}, ν_{NO_2})

Infrared and Raman spectra of p- and o-substituted phenols, thiophenols and their MR_n analogues in nonpolar solvents and solvents of different coordinating ability were recorded in the ν_{CO} and ν_{NO_2} regions [13–15]. Similar

spectral effects, both inter- and intramolecular, have been established for hydrogen and coordination bonds. The lower frequency bands of the bonded groups on formation of intermolecular hydrogen and coordination bonds are well marked, $\Delta\nu = 15$–40 cm^{-1}. The increasing concentration of p-substituted compounds (self-association) or the addition of a coordinating solvent (hetero-association), as well as a temperature decrease, result in an increase in the relative intensity of the bonded groups band and a decrease in the intensity of ν_{free} vibrations. This is particularly striking for carbonyl-containing compounds (e.g., Fig. 1) [13]. Addition of coordinating solvents to solutions of compounds with *ortho*-C(=O)R and NO$_2$ group either gives rise to higher frequency bands for the free groups or leads to an increase in intensity for both the organic compounds and their MR$_n$ counterparts. Thus, the cleavage of intramolecular hydrogen and coordination bonds results in spectral changes of the same type [14, 15].

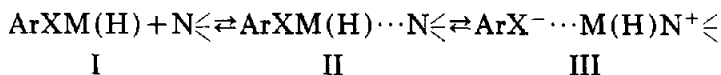COMPARISON OF PROTON AND ORGANOMETALLIC CATION TRANSFER PROCESSES

The common character of spectral effects upon molecular complexes, ionic pairs and ion formation with hydrogen and coordination bonds in isostructural systems has been established. The equilibria observed in the solutions may be useful for the interpretation of potential energy surface for a proton and a organometallic cation transfer.

Interaction with N- and P-bases

We examined the interaction of a series of XH acids and their MR$_n$ analogues (*o*- and *p*- nitrothiophenols, nitroanilines and nitrophenols, some of them also including the additional acceptor substituents) with amines (Py, Et$_3$N, Et$_2$NH) by means of UV spectroscopy coupled with IR data.

The spectral criteria which enable one to detect various types of complexes based on the values of the red shifts of longwave bands for nitrophenols have been proposed previously [16, 17]. We have proved their fitness for both the S and N analogues, and for organometallic derivatives. The formation of molecular complexes (m.c.) is accompanied by small shifts, $\Delta\lambda = 15$–20 nm; on formation of ionic pairs the shifts are far more pronounced, $\Delta\lambda = 60$–120 nm [18].

A general pattern of interaction with N-bases may be depicted by the equilibrium:

$$\text{ArXM(H)} + \text{N} \lessgtr \rightleftharpoons \text{ArXM(H)} \cdots \text{N} \lessgtr \rightleftharpoons \text{ArX}^- \cdots \text{M(H)N}^+ \lessgtr$$

$$\text{I} \qquad\qquad \text{II} \qquad\qquad \text{III}$$

It has been found that for the XH acids and their MR$_n$ derivatives, the in-

fluence of medium, ring substituent, donor capacity of amine and heteroatom X on the type of equilibrium is the same in both cases. For these analogous cases three types of equilibria are possible:
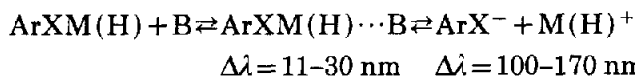
$$I \rightleftarrows II, \qquad I \rightleftarrows II \rightleftarrows III, \qquad I \rightleftarrows III$$

For instance, in the course of interaction of p-nitrophenol and its organometallic counterparts with Py and Et_3N in benzene equilibrium $I \rightleftarrows II$ prevails [17, 18]. An increase in donor properties of amine (Et_2NH) or polar properties of the solvent (CH_2Cl_2) gives rise to ionic pairs along with the formation of molecular complexes ($I \rightleftarrows II \rightleftarrows III$). In acetonitrile, the formation of ionic pairs with Et_3N does not require stage II (equilibrium $I \rightleftarrows III$). One may observe the same equilibrium type in inert medium with the introduction of electron–acceptor substituents into the ring or replacement of a heteroatom X for S and N (SO_2Ph). It is of interest to note that the types of complexes formed for XH acids and their MR_n derivatives are the same in all instances [18]. Quantitative estimation of such interactions, namely formation constants for molecular and ionic type complexes, K_c and $K_{i.p.}$, respectively, revealed that the capacity of metals (XM bonds) for interaction with amines is lower than that of a hydrogen atom (XH bonds) (Table 2).

As expected, replacement of "hard" N-bases, i.e. containing more electronegative and less polarizable atoms, with "soft" P-bases [19] causes the inversion of the capacity of "hard" XH acids and "soft" MR_n derivatives for coordination interactions [20]. Interaction of the latter with a "soft" P-base gains strength compared with "hard" N-bases, whereas that of "hard" XH acids slows down, which is consistent with the Pearson principle [19]. During the interaction of organometallic compounds with PPh_3, the former undergo ionization in an inert medium, avoiding the stage of complex formation (equilibrium $I \rightleftarrows III$). Under the same conditions, XH acids form only weak molecular complexes with a phosphorus atom. These do not produce any spectral changes; the IR spectra equilibrium $I \rightleftarrows II$ (Table 2).

Interaction with oxygen-containing bases (DMSO, HMTAP)

The character of interaction with "hard" polar O-bases is quite different from that with N- and P-bases, and is the same for XH and XMR_n groups. As has been proved by combination of UV spectroscopy and conductometry measurements [21, 22], the stage of molecular complex formation is necessary; then dissociation follows without going through ionic pair formation:

$$ArXM(H) + B \rightleftarrows ArXM(H) \cdots B \rightleftarrows ArX^- + M(H)^+$$
$$\Delta\lambda = 11\text{–}30 \text{ nm} \qquad \Delta\lambda = 100\text{–}170 \text{ nm}$$

For all organometallic derivatives under investigation, the capacity to form complexes is lower than that of the corresponding XH acids, with the exception

TABLE 2

The constants of molecular complexes and ionic pair formation[a] upon interaction with N-bases and triphenylphosphine

(a) $4\text{-}NO_2C_6H_4OMR_n$ + pyridine in benzene

Group	K_c	Group	K_c
OH	99	SH	0.25
OSnPh$_3$	17.3	SPbPh$_3$	0.13
OPbPh$_3$	25.1	SHgPh	1.04
OHgPh	0.98		
OSbPh$_4$	0.09		

(b) $ArXMR_n + NEt_3$ (PPh$_3$)

Compounds	Benzene		Dichlorethane		Acetonitrile
	K_c	$K_{i.p.}$	K_c	$K_{i.p.}$	$K_{i.p.}$
$4\text{-}NO_2C_6H_4OH$	1600	0 (0)	0.68	440	240
$4\text{-}NO_2C_6H_4OSnPh_3$	15	$-$ (1.0)	0.5	230	
$4\text{-}NO_2C_6H_4OHgPh$		$-$ (120)			
$4\text{-}NO_2\text{-}2ClC_6H_4OH$	0	1400	0	45×10^3	15×10^4
$4\text{-}NO_2\text{-}2ClC_6H_3OHgPh$	0	30	0	350	25×10^3
$4\text{-}NO_2C_6H_4N(SO_2Ph)H$	0	25 (0)	0	246	5×10^2
$4\text{-}NO_2C_6H_4N(SO_2Ph)HgPh$	0	0.7 (11)	0	25	

[a]K_c and $K_{i.p.}$ are in units of l mol^{-1}.

of SHgPh. In the case of oxygen-derivatives, the value of K_c decreases in the series (Table 3):

$$ArOH > ArOPbPh_3 > ArOSnPh_3 \gg ArOHgPh > ArOSbPh_4$$

The first three compounds form stable complexes with $K_c > 100$. The sequence of the K_c values for nitroanilines and their PhHg-derivatives is the same: $ArNRH > ArRHgPh$ [23]. As far as thioanalogues are concerned, in accordance with the lower bond polarity the values of K_c for stable complexes decrease by two orders of magnitude. The differences between separate compounds are leveled, and the sequence of the values of K_c changes:

$$ArSHgPh > ArSH > AsSSbPh_2 > ArSPbPh_3 > ArSSbPh_4 \geqslant ArSSnPh_3$$

A noteworthy feature is that the sequence of K_c is not base dependent. The same sequence has been reported previously for interaction with Py and HMTAP; the only addendum is that for Py the K_c values are reduced by approximately an order of magnitude whereas in the case of HMTAP these are 2–5 times greater than for DMSO.

Comparison of K_c values for the corresponding *para-* and *ortho-* (NO$_2$ or COR) compounds was used to estimate the stability of chelate cycles formed

TABLE 3

Constants of complex formation with DMSO and dissociation to ions in DMSO for the compounds $NO_2C_6H_4XMR_n$ (25°C)

XMR_n	K_c ($l\,mol^{-1}$)	$K_d \times 10^6$ ($mol\,l^{-1}$)	XMR_n	K_c ($l\,mol^{-1}$)	$K_d \times 10^6$ ($mol\,l^{-1}$)
4-NO₂					
OH	790	0.2	SH	1.6	4.7
OSnPh₃	140	7.0	SSnPh₃	0.7	17.0
OPbPh₃	230	90.5	SPbPh₃	1.2	0.4
OHgPh	1.4	10	SHgPh	3.9	<0.01
OSbPh₄	0.5	400	SSbPh₄	0.8	3300
NHSO₂Ph	432	8.0	SSbPh₂	1.4	0.3
NHgPhSO₂Ph	6.1	14.0			
2-NO₂					
OH	0.1	0.15	SH	0.5	2.9
OHgPh	0.9	17.0	SHgPh	3.3	<0.01
			SPbPh₃	0.8	0.5

by Hg and Pb atoms. The analysis of the ratio of constant values, K_{para}/K_{ortho}, led us to conclude that the stability of intramolecular coordination bonds is close to that of a weak intramolecular hydrogen bond in o-nitrothiophenols (<1 kcal mol^{-1}) [15].

As can be inferred from Table 3, the sequences of the values of dissociation constants, K_d, for XM bonds differ substantially from those given above for complex formation constants:

ArOSbPh₄ > ArOPbPh₃ > ArOHgPh > ArOSnPh₃ > ArOH

ArSbPh₄ > ArSSnPh₃ > ArSH > ArSPbPh₃, ArSSbPh₂ ≫ ArSHgPh

In some instances, the variations in K_c and K_d are anti-parallel. In other words, the relative capacity for XH and XM bond dissociations is not determined by the force of the coordination interactions.

THE POLARITY OF XH AND XM BONDS IN DIFFERENT MEDIA; ANALYSIS OF THE RELATIONSHIP BETWEEN THE POLARITY OF THESE BONDS AND THEIR CAPACITY FOR COMPLEX FORMATION AND DISSOCIATION

We have proposed to estimate the relative polarities of XM and XH bonds on the basis of the integral intensities of the symmetric vibrations of the p-nitro group in the IR spectrum (A_sNO_2). The rationale for such an approach

is as follows. Linear correlations between the values of $\Sigma\,A_sNO_2$ * and A_{Ar} are found. The latter are known to be sensitive to such intermolecular interactions as conjugation of a lone electron pair with a ring [25]. However, according to our data, the sensitivity of $\Sigma\,A_sNO_2$ to an increase of conjugation on replacing an H atom for a MR_n group is 2–3.5 times as great as that of A_{Ar} [26].

The main point here is that an increase of A_sNO_2 for various organometallic groups, provided the organic ligands remain the same, can be determined only via a shift of the electron density from the metal atom; it therefore, corresponds to an increase in the polarity of the XM bond [27].

As can be seen from Table 4, the values of A_sNO_2, which represent the polarity of the bonds, on passing from XH to XM increase in the series:
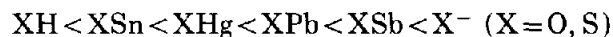
$$XH < XSn < XHg < XPb < XSb < X^- \quad (X = O, S)$$
$$XH < XHg < X^- \quad (X = NH)$$

TABLE 4

The integral intensities of the ν_{Ar} (1600) and ν_SNO_2 bands, $A \times 10^{-4}\,l\,mol^{-1}\,cm^{-2}$, for the compounds $4\text{-}NO_2C_6H_4XMR_n$

	C_6H_6		DMSO	
	ΣA_sNO_2	A_{Ar}	ΣA_sNO_2	A_{Ar}
SH	1.9	1.0	2.3	1.7
SSnPh$_3$	2.5	1.3	3.6	2.2
SPbPh$_3$	3.3	1.6	4.4	3.3
SH$_g$Ph	3.8		4.1	2.6
SSbPh$_4$	4.2	2.2	21.0	4.2
S$^-$	14.2[a]		21.0	
OH	4.9	2.2	8.4	3.3
OSnPh$_3$	11.0	3.9	18.1	4.8
OPbPh$_3$	13.0	3.6	26.8	
OHgPh	8.0	3.1	22.0	5.0
OSbPh$_4$	13.7	4.9	28.0	
O$^-$	19.0[a]		37.5	
NH(SO$_2$Ph)	6.5	2.1	7.0	2.5
NHgPh(SO$_2$Ph)	6.7	2.6	7.6	3.0
N(SO$_2$Ph)$^-$	15.6[a]		32.0	
NH$_2$	9.2	4.0	12.5	4.5
NHHgPh	13.2	5.7	26.4	6.8
NH$^-$	29.2[a]		72.1	

[a]The A_sNO_2 values for the anions in C_6H_6 were determined from the correlation equations.

*The IR spectra of the solutions of p-nitrophenol and p-nitroaniline derivatives exhibit two bands, the intensities of which are determined by the contribution of the ν_sNO_2 vibrations [24]. Therefore, as the νNO_2 intensity one should take the total intensity of both components of the doublet.

The bond polarity in polar and coordinating solvents is more pronounced than in "inert" ones (CH_2Cl_2, C_6H_6). Linear relations have been separately established between the values of $A_sNO_2^{1/2}$ in CH_3CN (DMSO) and C_6H_6 for compounds of types ArXH, $ArXMR_n$ and AX^-. Figure 2 gives a clear indication of the relative polarities of the bonds, in terms of closeness to the purely ionic one (X^-), in a given solvent. It also defines sensitivity of the polarity to the influence of the medium ($CH_3CN < DMSO$) depending on X ($N > O > S$).

What is the relationship between the coordination or dissociation capacity and polarity in the case of XH acids and their MR_n derivatives? In the case of XH acids, the capacity to form hydrogen bonds varies in parallel with the polarity in coordinating solvents ($OH > NH > SH$). As far as organometallic compounds are concerned, only in the case of compounds whose complexing capacity varies within a wide range do the variations in K_c and polarity run in parallel (the derivatives of Group IV elements):

$$OPb > OSn > SPb > SSn$$
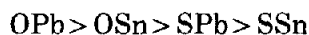
The remaining MR_n derivatives are weak Lewis acids and there is no correlation between polarity and coordination capacity.

Our findings indicate that there is a close relationship between XH or XM bond polarity and the capacity of these bonds for dissociation. Linear correlations have been established between $\log K_d$ and ΣA_sNO_2 for each class of compound, the points for XH acids and MR_n derivatives lying on a straight

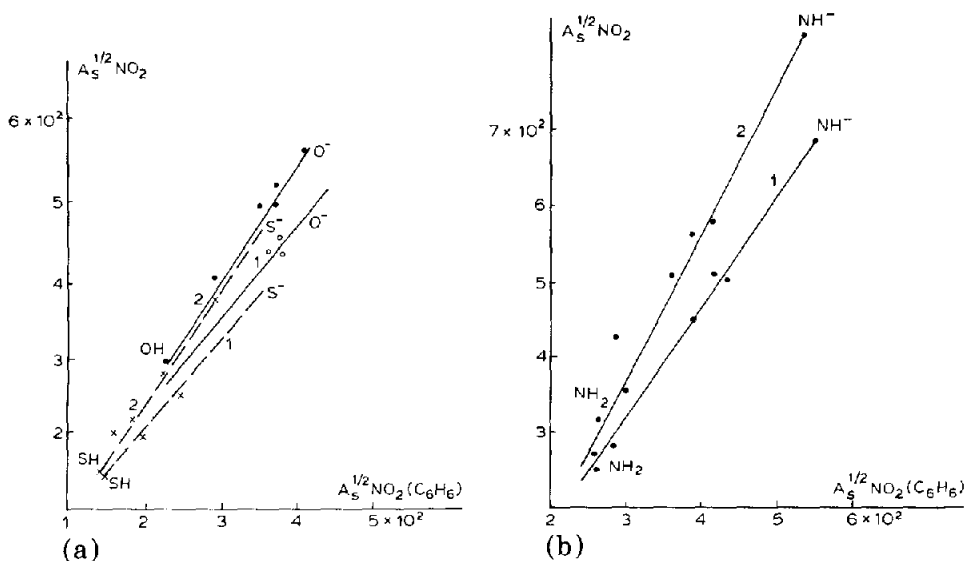Fig. 2. Linear correlations between the integral intensities A_sNO_2 in coordinating solvents: CH_3CN (1), DMSO (2) and C_6H_6 for compounds of the ArXH, $ArXMR_n$, AX^- types ($r = 0.96 - 0.99$). (a) X = O, S; (b) X = NR.

line [27]. The abnormal stability of the bonds of the "soft" groups with a "soft" heteroatom (S–Hg, S–Pb) is consistent with the Pearson principle.

Thus, the cleavage of XH and XM bonds appears to be controlled by their polarity but not their capacity for coordination interactions with a solvent. Neither qualitative differences between the behaviour of XH acids and their XMR_n derivatives nor differences in spectral changes with formation of hydrogen and coordination bonds of the molecular and ionic type have been detected. Linear relations between the relative bond polarity (the values of A_sNO_2) in different solvents as well as between the polarity in DMSO and the capacity for ionic dissociation indicate that the points corresponding to XH and XM bonds fall on the same straight lines.

Summing up the comparison of isostructural systems involving hydrogen and coordination bonds, one may say that, in spite of the great size and polarizability of MR_n groups, the comparison does not reveal the uniqueness of hydrogen bond. This conclusion is in accord with the profound similarity in some properties of the H atom and the MR_n groups under consideration.

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