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Structural and electronic responses of coordination compounds to changes in the molecule and molecular environment

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CONTENTS

A. INTRODUCTION

According to quantum mechanics, charge transfer is involved in any molecular interaction. This means that one of the reacting species may be considered as a donor of electronic charge and the other one as an acceptor of electronic charge. Any changes within the charge density pattern involve changes in the positions of the nuclei, associated with changes in bond lengths and changes in bond angles, which, in principle, extend over the whole system under consideration.

Despite the enormous variety of such changes, simple rules have been formulated. The bond length variation rules [1], also referred to as Gutmann rules [2],

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are based on qualitative observations and quantitative results and are in agreement with quantum chemical requirements and results. These rules are independent of model assumptions about bonding forces and are applicable to σ-interactions [1].

B. THE FIRST BOND LENGTH VARIATION RULE AND THE "PILE UP" AND "SPILL OVER" EFFECTS

The first bond length variation rule states that an intermolecular interaction leads to lengthening of the intramolecular bonds which are adjacent to the site of the intermolecular interaction [1]. The shorter the intermolecular distance D→A, the greater is the lengthening of the adjacent intramolecular bonds both in the donor and acceptor components (Fig. 1).

Inverse relationships between intermolecular and intramolecular bond length are well demonstrated by the results of X-ray analyses of different crystalline hydrates [3] (Fig. 2).

The increase in internuclear distances is indicated by a full bent arrow pointing in the direction of the charge transfer between the two considered atoms. The effects are exemplified by the interaction between nitrogen donors and BF_3 as shown in Fig. 3 and in Table 1.

Bond lengthening is associated with an increase in bond polarity [4] and hence with increasing fractional charges of the bonded atoms. Experimental evidence, as well as results of quantum-chemical calculations, reveals that both the negative net charge of the donor atom and the positive net charge of the acceptor atom are usually increased. The loss of negative charge at the donor atom due to interaction with the acceptor is overcompensated by the induced attraction of negative charge

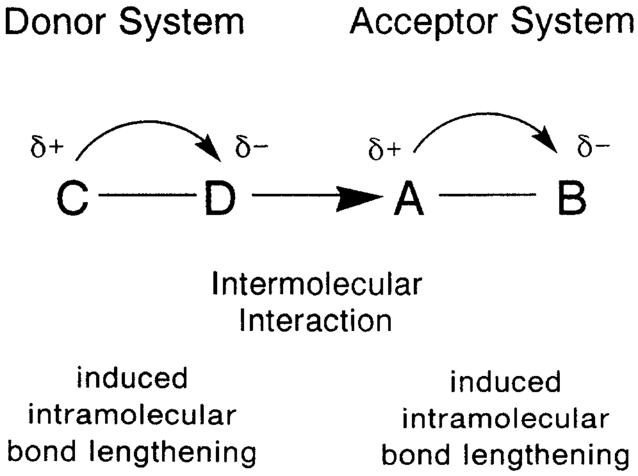


Fig. 1. General scheme of the interaction between a donor system (C—D) and an acceptor system (A—B) via the donor atom (D) and the acceptor atom (A).

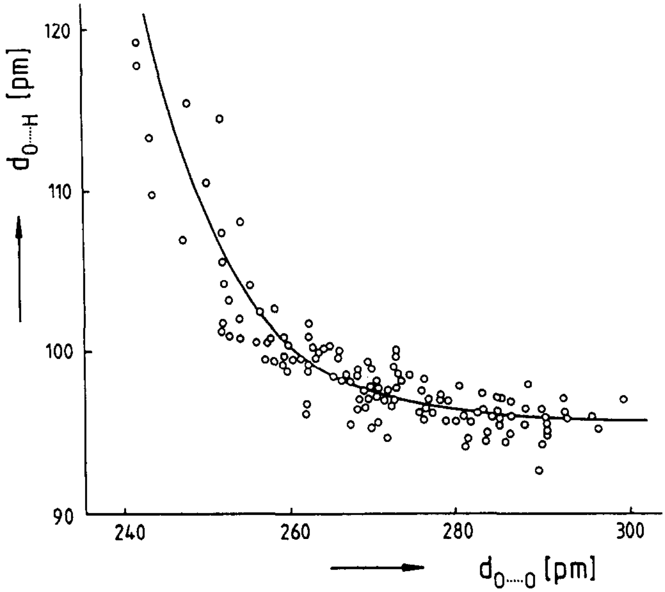


Fig. 2. Relationship between intermolecular O···O distances and intramolecular O···H distances in crystalline hydrates.

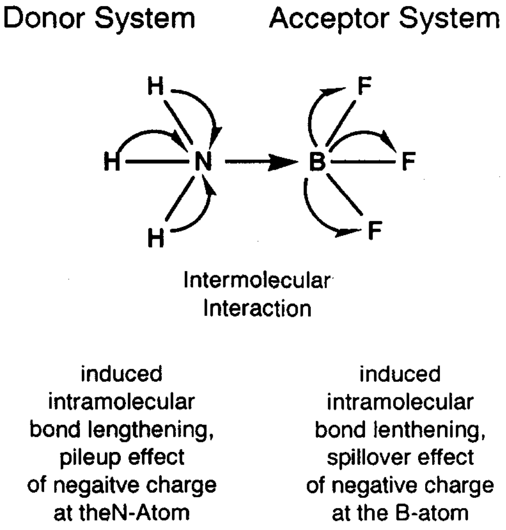


Fig. 3. Donor–acceptor interaction of NH_3 with BF_3.

from the other atoms of the donor unit. This is called the *pile up effect* of net charge at the donor atom [1,5]. On the other hand, charge transfer to the acceptor atom is overcompensated in the latter by the induced flow of negative charge from the acceptor atom towards the peripheral atoms. This leads to an increase of positive

TABLE 1

Changes in intramolecular B–F bond length and F–B–F bond angle as related to the intermolecular N–B distances

Compound	Intermolecular N–B distance (pm)	Intramolecular	
		B–F distance (pm)	α_{F-B-F}/deg
BF_3	–	130	120
CH_3CN-BF_3	163	133	114
H_3N-BF_3	160	138	111
$(CH_3)_3N-BF_3$	158	139	107

charge of the acceptor atom and of negative charge of the peripheral atoms and is referred to as the *spill over effect* of negative charge at the acceptor atom [1,5].

These effects are essential requirements for the course of the ionization of a covalent substrate. For example, the representation of a nucleophilic substitution by an amine in organic chemistry by assigning an increase in positive charge to the nitrogen atom of the amine is therefore not correct. It is true that the whole amine molecule becomes more positive, but the nitrogen atom becomes more negative!

These considerations are not confined to Lewis acid–base interactions but may be applied to other types of molecular interactions. For example, in the iodine molecule in the gas phase, the mean intramolecular distance is 268 pm and the mean intermolecular distances are extremely long. However, in the crystal, because of the relatively short mean intermolecular distance of 345 pm, the mean intramolecular distance is increased to 272 pm. Under pressure, the intermolecular distance is further decreased and consequently the intramolecular distance increased, until all I—I distances are equally long (287 pm) [1].

The so-called pressure distance paradox expresses the fact that increase in pressure causes lengthening of chemical bonds in crystals, although at the same time the density is increased, and hence the volume available for the atoms is decreased. The solution to this paradox is as follows: The "intermolecular" distances (e.g. in silicon dioxide the O—O and Si—Si distances) are commonly not considered as chemical bonds and they are shortened to a great extent, so that the intramolecular distances, commonly denoted as chemical bonds (e.g. in SiO_2 the Si—O distances) are lengthened according to the bond length variation rules. The transformation of coesite (SiO_2) into stishovite (SiO_2), is accomplished at 100 kbar and 1200°C. As the density increases from 2.93 to 4.28 g cm^{-3}, the intermolecular distances are considerably shortened, namely the Si—Si distances from 301 pm in coesite to 267 pm in stishovite and the O—O distances from 263 to 251 pm, respectively. Consequently, the Si—O bond lengths are increased from 161 pm in coesite to 178 pm in stishovite. A further, well-known example of this paradox is the transition of graphite into diamond. The C—C distances in diamond are greater that those within the graphite layers. The increase in density in going from graphite to diamond is associated with the considerable shortening in the interlayer distances initially present in graphite [1] and hence with a slight lengthening of the C—C distances, formerly within the layers.

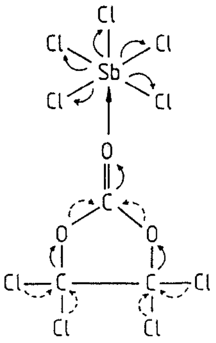
Because the molecules at a surface of a condensed phase (solid or liquid) have smaller coordination numbers than within the bulk of the phase, a bond shortening at a surface has, for a long time, been unacceptable. In 1928, Lennard-Jones [6] predicted that lattice parameters near and perpendicular to the surface should be smaller than those within the crystal lattice. Due to the lack of experimental techniques, no experimental evidence was found for a long time but 50 years later, the low-energy electron diffraction method allowed its confirmation. The results revealed, for example, that the mean internuclear distances in silver(111) surface planes are about 6% smaller than those within the crystal.

The first bond length variation rule may also be formulated in terms of changing coordination numbers: As the coordination number is increased, the length of the bonds originating from the coordination centre is increased, in agreement with the old Goldschmid rule [7] for solid state systems.

C. THE SECOND BOND LENGTH VARIATION RULE

The second bond length variation rule concerns the description of changes in bond lengths in all other regions within the newly formed molecular system. It states that bond lengthening occurs when negative charge is shifted from a more electropositive towards a more electronegative atom (in agreement with the first rule) and that bond shortening takes place when negative charge is shifted from a more electronegative towards a more electropositive atom. Bond polarity and bond length are increased in the first case, but decreased in the second. A broken line arrow is used to indicate a charge transfer associated with shortening of a bond associated with its strengthening (Fig. 4).

Alternating bond lengthening and bond shortening is found in those molecules in which atoms of higher and lower electronegativities are arranged in alternating sequences. This may be illustrated by the interaction of antimony pentachloride ($SbCl_5$) with tetrachloroethylenecarbonate [8] (Fig. 4). According to the first bond length variation rule, the (intramolecular) bonds, which are adjacent to the intermolecular O→Sb bond, namely the —C=O bonds and the Sb—Cl bonds, are lengthened (electron shift from the more electropositive towards the more electronegative atom) whereas the neighbouring O—C bonds are shortened (electron shift from the more electronegative to the more electropositive atom). The adjacent C—O bonds are lengthened and, in the peripheral regions of the donor component tetrachloroethylenecarbonate, both the C—C bonds and the C—Cl bonds are shortened as negative charges from the chlorine atoms are shifted towards the peripheral regions



Bond	Bond lengths in the isolated molecules [pm]	Bond lenghts in the adduct [pm]
Sb—Cl intermol.	231-243	235-247
C=O	115	122
O—C	133	125
C—O	140	144
C—C	153	143
C—Cl	176	174

Fig. 4. Bond lengths in free and in coordinated antimony pentachloride and tetrachloroethylene carbonate.

of the acceptor molecule ($SbCl_5$), thereby increasing the negative charges of the terminating (chlorine) atoms.

In the following text, the bond length variation rules as well as pile up and spill over effects will be further exemplified.

D. VARIATIONS IN BOND ANGLES

For the variations of bond angles, the following considerations have been made: In agreement with the Gillespie–Nyholm rules [9], coordination of the donor molecule leads to a "replacement" of a lone electron pair by a coordinate bond and hence to an increase of the adjacent bond angles in the donor system, whereas coordination at the acceptor molecule leads to the formation of a new bond and hence to a decrease of the bond angles in the acceptor molecule. This leads to the following rule: As the intermolecular interaction increases (Fig. 5) the intramolecular angles of the donor component (θ measured *opposite* to the attack of the acceptor unit) are increased and the intramolecular angles of the acceptor component (α measured *opposite* to the attack of the donor unit) are decreased. In other words, in the course of the donor–acceptor interaction, the atoms of the donor system which are adjacent

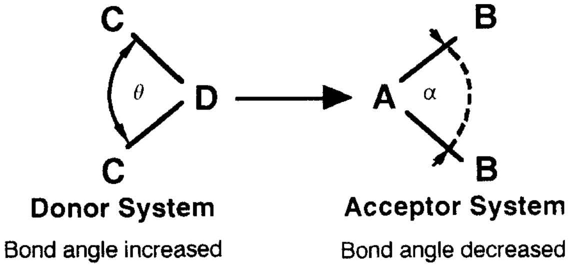


Fig. 5. Bond angle variation scheme for an interaction of a donor system with an acceptor system.

to the interaction site bend towards the acceptor system, while in the acceptor system the adjacent atoms bend away from the approaching donor system. The previously mentioned nitrogen donor–BF_3 system may be taken as an example for this rule, as can be seen from the α angles in Table 1, which decrease with decreasing intermolecular distance.

(i) Bond angle variation in trimethylchlorostannane

Another example is provided by trimethylchlorostannane in its interaction with a Lewis base molecule [10], whereby the tetrahedral molecule is converted into a trigonal bipyramid. Increasing donor strength of the base leads to lengthening of the Sn–Cl bond and to an increase in the negative charge at the chlorine atom [11]. Application of the above rules lead to the scheme (Fig. 6) which in turn is verified by spectroscopic, X-ray diffraction, and quantum chemical methods (MNDO-SCF calculations) [12].

In agreement with the first bond length variation rule, the frequency of the Sn–Cl stretching band is shifted linearly to lower values as the donor strength of the solvent is increased. Changes in the Cl–Sn–C bond angle can be calculated from the ratios of the intensities of the symmetrical Sn–C stretching band (I_{sym}) and the asymmetric Sn–C stretching band [13]. In poorly coordinating solvents such as *n*-hexane and carbon disulphide, $(CH_3)_3SnCl$ shows the same angle as in the gas phase [14]. In agreement with the above bond-angle variation rules, the Cl–Sn–C angle is decreased as the solvent donor number (DN) is increased. For HMPT, the strongest donor investigated, an angle of 94.3° is found, which is close to that of 95.7° reported for $(CH_3)_3SnCl{\cdot}HMPT$ in the solid state from X-ray diffraction data. A clear relationship is found between $\alpha_{\mathrm{C-Sn-Cl}}$ and the solvent DN (Fig. 7(a)), showing that the bipyramidal configuration is more closely approached as the donor strength of the solvent (acting as a ligand) is increased.

The plot of $\alpha_{\mathrm{C-Sn-Cl}}$ against the absorption frequency of the Sn–Cl stretching

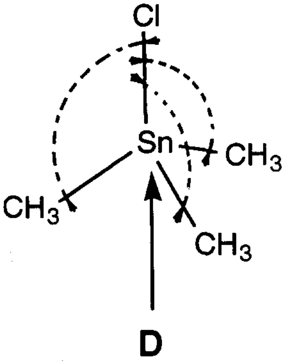


Fig. 6. Bond angle variation for a trimethylchlorostannane–donor system.

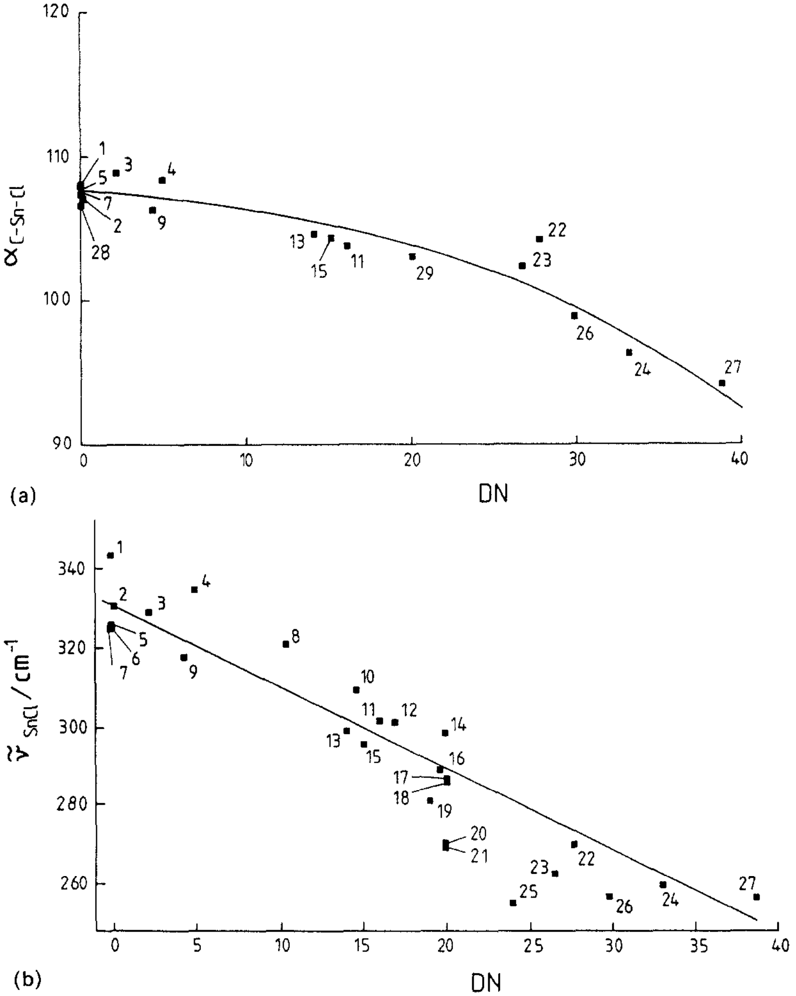


Fig. 7. (a) $\alpha_{C-Sn-Cl}$ calculated from the intensity ratio of symmetrical and asymmetrical Sn—C vibrations versus DN. (b) The relation with the Sn—Cl stretching vibration. 1 = *n*-Hexane; 2 = benzene; 3 = bromobenzene; 4 = CS_2; 5 = $CHCl_3$; 6 = CH_2Cl_2; 7 = 1,2-dichlorethane; 8 = acetic acid; 9 = nitrobenzene; 10 = dioxan; 11 = proprionitrile; 12 = acetone; 13 = acetonitrile; 14 = thetrahydrofurane; 15 = propandiolcarbonate; 16 = *n*-propanol; 17 = ethanol; 18 = *t*-butanol; 19 = methanol; 20 = i-propanol; 21 = i-butanol; 22 = *N*,*N*-dimethylacetamide; 23 = *N*,*N*-dimethylformamide; 24 = pyridine; 25 = formamide; 26 = dimethylsulphoxide; 27 = hexamethylphosphotriamide.

band depicted in Fig. 7(b) illustrates the mutual changes within the framework of both the first bond length variation rule and the bond angle variation rule. Clearly, the coordination by weakly donating solvent molecules is hardly developed, whereas in solvents of donor numbers of more than 20, the geometric changes are pronounced.

Figure 8 shows this in terms by the relation between the Sn—Cl bond length

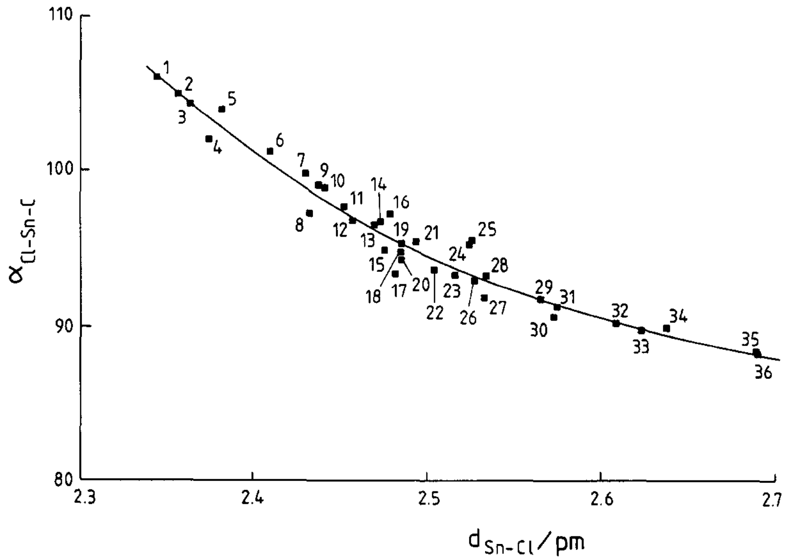


Fig. 8. Sn—Cl distances versus Cl—Sn—C angles in the solid state as found from X-ray diffraction (for details see refs. 12 and 13). 1 = Chloro-tris(tricarbonyl-$\sigma\eta^5$-cyclopentadienylmanganese)tin; 2,3 = chlorotriphenyltin; 4,10 = bis(chlorodiphenylstannyl)methane; 5 = trisbis(trimethylsilyl)methyl)chlorotin; 6 = chlorotricyclohexyltin; 7 = chlorotrimethyltin; 8,32 = (μ_2-methylene)-(chlorodiphenyltin)-(chlorodiphenylhexamethylphosphoramide-O)tin; 9,24 = (μ_2-pyrazine-N,N')-bis((μ_2-methylene)-dichlorotetramethyl-di-tin); 11 = chlorodimethyl-(2-(diphenylphosphinoyl)phenyl)tin; 12,14 = (μ_2-methylene)-(μ_2-pyridazine-N,N')-dichlorotetramethyl-di-tin; 13,35 = (μ_2-methylene)dichlorotetramethyl-2-pyridyl-di-tin; 15 = *m*-bis(diphenylphosphinyl)ethane-2-bis(chlorotriphenyl-tin); 16,30 = 3,3-bis(chlorodimethyltin)propylethylsulphoxide; 17 = chloro(1-((4′-methylphenylimino)methyl)-2-naphthol)triphenyltin-1-((4′-methylphenyl)-imino)methyl-2-naphthol; 18 = μ_2-(rac-1,2-bis(*n*-propylsulphinyl)-ethylene)-2-(O,O')-bis(chloro-*cis*-triphenyltin); 19 = (ε-caprolactam-*O*)chlorotriphenyltin; 20 = chloro-tetramethylureatriphenyltin; 21 = (3-(*t*-butyl(phenyl)phosphino)propyl)chlorodimethyltin; 22 = 3-(2-(1,10-phenanthrolyl))-5,6-diphenyl-1,2,4-triazinechloro-aquatriphenyltin; 23 = chlorotriphenyl-(pyridinium-2-carboxylato)tin; 25 = chlorotrimethyl(hexamethylphosphamide)tin; 26 = chlorotriphenyl(quinolinium-2-carboxylato-*O*)tin monohydrate; 27 = (μ_2-1,2-bis(diphenylarsoryl)ethane-O,O')bis(chlorotriphenyltin); 28 = chloro(2,6-dimethyl-pyridine-*N*-oxide)trimethyltin; 29 = chlorotrimethyl(triphenylphosphoranylidene-acetone)tin; 31 = benzyltriphenylphosphonium dichlorotributyltin; 33,34 = bis(μ_3-sulphido)-bis(bis(triphenylphosphine)gold)gold(I)dichlorotrimethyltin; 36 = benzyltriphenylphosphonium dichlorotributyltin.

and the Cl—Sn—C angle as obtained by X-ray diffraction data. Changes in the charge distributions and geometries for a series of adduct molecules have been calculated by means of quantum mechanical methods. The results are in good agreement with the results from electron diffraction [14], X-ray diffraction [15] and IR experiments [12]. All these experimental and theoretical results show that a continuous set of molecular geometries exists between tetrahedral and trigonal bipyramidal arrangement and that the bipyramidal form is approached more closely as the solvent DN is increased.

The interaction of $(CH_3)_3SnCl$ with Cl^- leads to increasing polarization of the original Sn—Cl bond, i.e. to a transfer of negative charge towards the Cl^- with considerable lengthening of this bond, until equal bond lengths for both Sn—Cl bonds and a C—Sn—Cl angle of 90° is reached. These effects are in accordance with the spill over effect (Q_{Sn}) and the pile up effect (Q_{Cl}) and the bond length variation rules. With decreasing Cl^-—Sn distance, the positive charge at the tin atom is increased, the charge at the originally bound chlorine atom is shifted to more negative values, again indicating the spill over effect at the acceptor atom as well as the pile up at the Cl atom. The total energy is decreased until its minimum at equal $d_{Cl^- \to Sn}$ and d_{Sn-Cl} distances is reached. The calculated dependence of d_{Sn-Cl} is similar to the distances found experimentally in the crystalline state and is the same as in $(CH_3)_3SnCl{\cdot}Cl^-$ (see Table 2) [12].

(ii) Bond angle variation in tetranuclear Cu(II) complexes

The bond angle variation rule is applicable to μ_4-oxo-hexa-μ_2-chlorotetrakis-(benzimidazole) copper(II) [16]. The molecule has a distorted tetrahedral structure [16] of copper(II) atoms located around a μ_4-oxide ion. Above each of the six edges are located μ_2 chloro-bridges. The structure is completed by four benzimidazole ligands bonded one to each copper atom by a nitrogen atom. The geometry around the copper atoms is trigonal bipyramidal with oxygen and nitrogen atoms in axial positions and three chlorine atoms in the equatorial plane (Fig. 9).

One of the equatorial Cu—Cl distances is considerably longer than the others and the equatorial Cl—Cu—Cl angle *opposite* the longer Cu—Cl bonds is smaller the shorter the latter. An almost linear correlation is found between the equatorial Cu—Cl bond length and the *opposite* Cl—Cu—Cl angle in the range between 235.2 pm and 251.5 pm and between 101° and 137°, respectively.

TABLE 2

MNDO results for decreasing distance of Cl^- acting as a donor towards the Sn atom in $(CH_3)_3SnCl$

$d_{Cl^- \to Sn}$/Å	d_{Sn-Cl}/Å	Q_{Sn}	Q_{Cl^-} [a]	Q_{Cl}	$\alpha_{C-Sn-Cl}$	E/kJ mol^{-1}
4.00	2.36	0.400	−0.994	−0.452	103.2	−107.9
3.80	2.36	0.411	−0.987	−0.465	102.5	−108.3
3.60	2.37	0.424	−0.974	−0.483	101.4	−108.8
3.40	2.38	0.439	−0.952	−0.506	99.9	−109.8
3.20	2.40	0.452	−0.914	−0.537	98.0	−111.6
3.00	2.41	0.458	−0.860	−0.565	97.0	−115.0
2.90	2.43	0.462	−0.828	−0.585	95.8	−117.0
2.80	2.44	0.465	−0.793	−0.605	94.6	−119.3
2.70	2.46	0.467	−0.755	−0.625	93.3	−121.3
2.60	2.48	0.468	−0.709	−0.656	90.6	−122.8
2.50	2.50	0.467	−0.669	−0.676	89.2	−123.6

[a] Cl^- represents the chlorine atom acting as a donor towards $(CH_3)_3SnCl$.

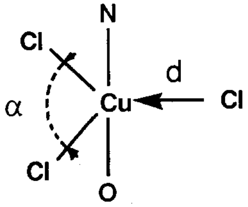


Fig. 9. Intramolecular bond angle variation for different Cu—Cl distances in the tetranuclear μ_4-oxo-hexa-μ_2-chlorotetrakis(benzimidazole)copper(II) complex.

E. EFFECTS AT THE TERMINAL POSITIONS

Studies of the bond energies in crystals and in solutions have revealed that the electronic changes are well pronounced in the terminal regions of the system under consideration. For example, Singh and Tedder [17] found an increase in rate of chlorination of carboxylic acids in the presence of acceptor molecules which is greatest at the C—H group terminating the chain.

The results obtained for the interactions of NH_3 with boranes carrying linear alkyl substituents of varying chain length confirm the great influence of the charge transfer at the donor and acceptor atoms, at the C_1 atom *and* at the terminating C atom [18]. Alternating changes in the charges are less pronounced in the middle of the carbon chain. The greatest changes are found at the terminating atoms which become more negative at the acceptor component (the boranes) and more positive at the donor component (the amines), in agreement with the bond length variation rules and spill over and pile up effects, respectively.

A convincing example for the pronounced effects at the end of the molecular chain is provided by haemoglobin, where two protons are released from the ends of the protein chain separated by a large number of atoms from the iron atom of the haeme groups as soon as oxygen is coordinated to the latter (see Sect. I(ii)).

F. SOLVENT AND SUBSTITUENT EFFECTS ON IRON–PHENANTHROLINE COMPLEXES

In tris(phenanthroline)iron complexes, the iron atom is surrounded by phenanthroline groups (phen), each of them bonded to the iron nucleus via the two nitrogen atoms. $[Fe(phen)_3]^{3+}$ is blue in colour, whereas $[Fe(phen)_3]^{2+}$ is red. It is usually assumed that the electron densities around the nucleus are greater in the red (the reduced) than that in the blue (the oxidized) form. Accordingly, iron is assigned to oxidation number +II in the red and +III in the blue complex. The differences in magnetic behaviour (the blue complex is paramagnetic, whereas the red complex is diamagnetic) are described by stating that the valence configuration is d^5 in the blue complex and d^6 in the red complex [19].

Redox changes can take place readily

$$\underset{\substack{\text{red,}\\ \text{reduced Form}\\ \text{diamagnetic}\\ d^6}}{\mathrm{Fe(phen)}_3^{2+}} \rightleftarrows \underset{\substack{\text{blue}\\ \text{oxidized Form}\\ \text{paramagnetic}\\ d^5}}{\mathrm{Fe(phen)}_3^{3+}} + e^-$$

Accordingly, the diamagnetism of the red form is regarded as being due to a pairwise arrangement of the six d-electrons and the paramagnetism of the blue form as due to the presence of five d-electrons. From these considerations, one might expect for the two forms different electron densities around the iron nucleus and hence different Fe–N distances. However, X-ray structural analysis does not show any differences [20]. The differences in electron density should be reflected in differences in the Mössbauer isomer shifts. It would be expected that the isomer shift in the blue form (smaller electron density) should be smaller than in the red form (greater electron density). In fact, hardly any differences are found between the two forms. Even with substitution at the phenanthroline rings, the Mössbauer isomer shifts remain nearly invariant [19,21]. A close examination of the results reveals that the small differences found in the Mössbauer isomer shifts indicate an even greater electron density in the oxidized than in the reduced form. Differences between these forms are found in the Mössbauer quadrupole splittings. They indicate differences in the electronic field gradients at the iron nuclei and hence differences in the differentiations within the charge density pattern. The results are in agreement with those obtained from the quantum chemical calculations [19]. The partial charges at the coordination centre are somewhat more positive in the reduced than in the oxidized species and in both cases are near to zero. According to the results of the calculations referred to, the charge differences between oxidized and reduced species are most pronounced at the terminating C–H groups. The peripheral hydrogen atoms have higher positive net charges in the oxidized than in the reduced form and for this reason the redox couple is not suitable as a reference system in different solvents [22,23].

In order to explain the experimental results on current grounds, it was found necessary to extend the usual descriptions by considering the π-electron distribution functions of the whole system. It is assumed that, due to the overlap of the three phenanthroline ligands together with t_{2g} d-functions of the iron coordination centre, new, energetically relatively low-lying π-acceptor regions occur: The system acts not only as a π-electron donor, but also as a π-electron acceptor towards both the coordination centre and other molecules. Strongly bound water molecules are found in the inter-ligand pockets which cannot be removed by heating or by reduced pressure without decomposition of the complex [19,20].

These findings suggest that the charge density pattern has highly developed adaptability towards changes with nearly invariant charge density around the iron nucleus. Thus, the d-electron densities are spread over the whole complex unit and cannot be considered as "located" near the coordination centre. The region around the iron nucleus appears to function as a "regulating centre" for electronic changes by which the charge density redistribution over the whole complex is effected. In order to describe these features, the concept of molecular system organization has been introduced [24] as indicated in the last section.

G. SPIN TRANSITION SYSTEMS

Most tris(phenanthroline) iron complexes are in "low-spin" states, and these are maintained in all solvents as well as after substitutions in the 3, 4, 5, 6, 7 or 8 positions. By all of these changes, the densities around the coordination centre remain nearly invariant. However, by substitution in the immediate neighbourhood of only one of the two phen-N atoms (i.e. either in the 2 or 9 position of the phenanthroline) the Fe—N distances no longer remain equal and a transition into the high spin state occurs. Thus the symmetry in electron distribution around the coordination centre cannot be restored unless the complex reaches a state of higher energy, i.e. the high spin complex. In passing from the low-spin state into the high-spin state, the system passes a state of greatest heat capacity associated with optimal differentiation [25].

Several iron(II) and iron(III) coordination compounds are known to show spin state equilibria between low-spin and high-spin states in solution. These are influenced both by change of solvent and by change in temperature and are accompanied by changes in colour. Reference is made to solvatochromic and thermochromic behaviour [26–29].

Tris(2-(aminomethyl)pyridine) iron(II) has been reported [26] to be the first known iron(II) system in solution in which the high-spin form is labile. The ratio of the low-spin to the high-spin species in solution increases linearly with increasing solvent donor number due to donor attack at the two acid protons at the aminopyridine ligands. The charge distribution and ligand field near the coordination centre is changed via intramolecular charge transfer during the course of the interaction [30] as depicted schematically in Fig. 10.

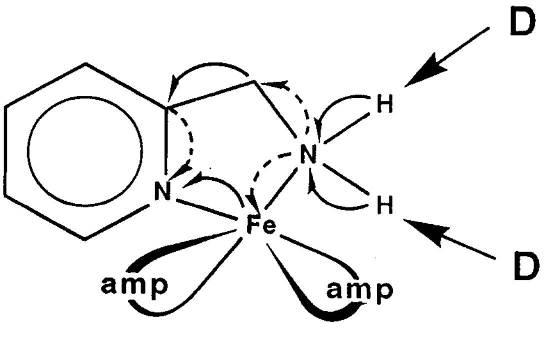


Fig. 10. Scheme of electron redistribution and bond length variation in Fe(amp)$_3$(Bϕ_4) induced by interaction of the amino protons with donor solvent molecules, D.

According to the bond length variation rules, the attack of a donor molecule at the amino protons leads to a shortening of the N—Fe bonds and hence to an increase in bond strength. A less pronounced lengthening of the Fe—N bonds of the aminopyridine nitrogen atoms should occur. These changes near the coordination centre lead to a destabilization of the high-spin state with increasing donor strength of the donor solvent, D. The protonation at the amino nitrogen atoms leads to a lowering of the energetically higher Fe—N stretching vibration associated with the amino nitrogen atom and to higher frequency of the Fe—N vibrations involving the pyridine nitrogen atoms [30]. This change in bond strength is also seen from X-ray results [31,32] and is found to be in agreement with the bond length variation rules.

H. SOLVATOCHROMISM OF COORDINATION COMPOUNDS

Several compounds are known to change their spectroscopic properties in different solvents within the visible region. So they may be used as colour indicators for the donor and acceptor properties of a solvent. Such systems will be presented in the following sections.

(i) Bis-cyano-bis-phenanthroline-iron complexes

$Fe(phen)_2(CN)_2$ (see Fig. 11) is known to act as a donor molecule via the nitrogen atoms of the CN groups (the C is coordinated towards the Fe-coordination centre) [33–35]. The interaction with acceptor solvents leads to solvatochromism

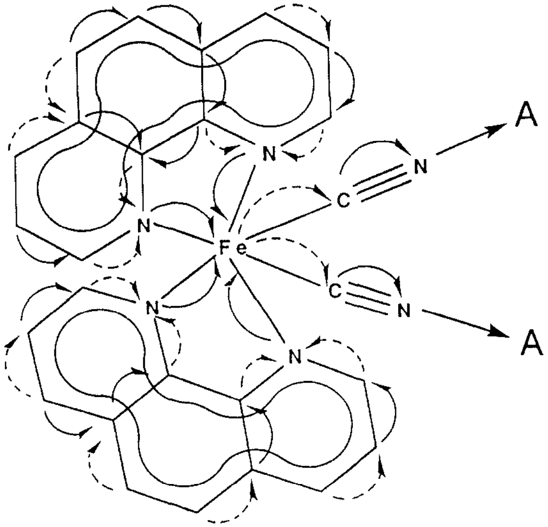


Fig. 11. Scheme of electron redistribution and bond length variation in $Fe(phen)_2(CN)_2$ induced by interaction of the amino protons with acceptor solvent molecules, A.

related to the acceptor strength of the solvent. Figure 12 shows a linear relationship between a charge transfer absorption band and the solvent's acceptor number and hence the complex may be used as a colour indicator for the estimation of the acceptor properties of solvents and of solvent mixtures and of solutions. Both the Fe(III) and the Fe(II) species show similar solvatochromism [34]. However, the coordination centre remains invariant, as can be seen from Mössbauer isomer shifts [24], so that the solvatochromic colour change must be related to changes in the ligand orbital system (most probably the π-acceptor orbitals).

(ii) Mixed-ligand copper and nickel complexes

Square planar Cu(II) complexes with a diamine and a β-diketone as ligands show solvatochromic properties which are governed by the donor properties of the respective solvent [33,36,37].

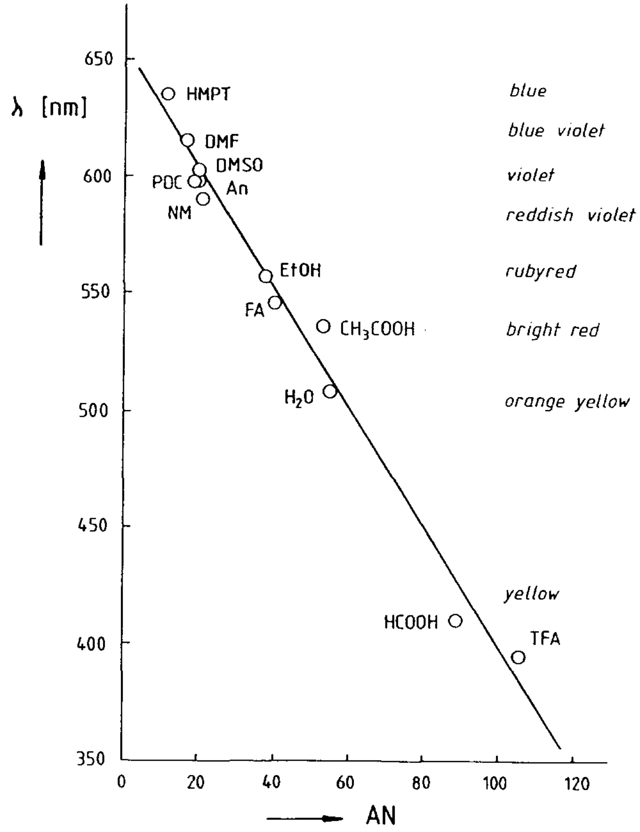


Fig. 12. Changes of wavelength of the charge transfer bands Fe(phen)$_2$(CN)$_2$ in solvents of different acceptor number (AN) [36].

$$[\mathrm{Cu}(\beta\text{-dike})(\mathrm{diam})]^+ + 2\mathrm{D} \rightleftarrows \underbrace{[\mathrm{Cu}(\beta\text{-dike})(\mathrm{diam})\mathrm{D}_2]^+}_{\substack{\text{continuous colour change from}\\ \text{red to green depending on the}\\ \text{donor strength of D}}}$$

The continuous colour shift depends on the donor strength of the coordinated ligands, D, and hence this complex may be used as a colour indicator for the donor properties of solvents, of solvent mixtures and of solutions. In fact, such copper complexes can be used as colour indicators, visualizing the donor properties of solvents [34, 36, 38] (see Fig. 13).

The solvatochromism of the corresponding Ni(II) compounds is also due to coordination of donor solvent molecules. In this case, however, the absorption maxima within the visible region of the analogous nickel compound are hardly changed [38–41]. The observed solvatochromism is based on the existence of only

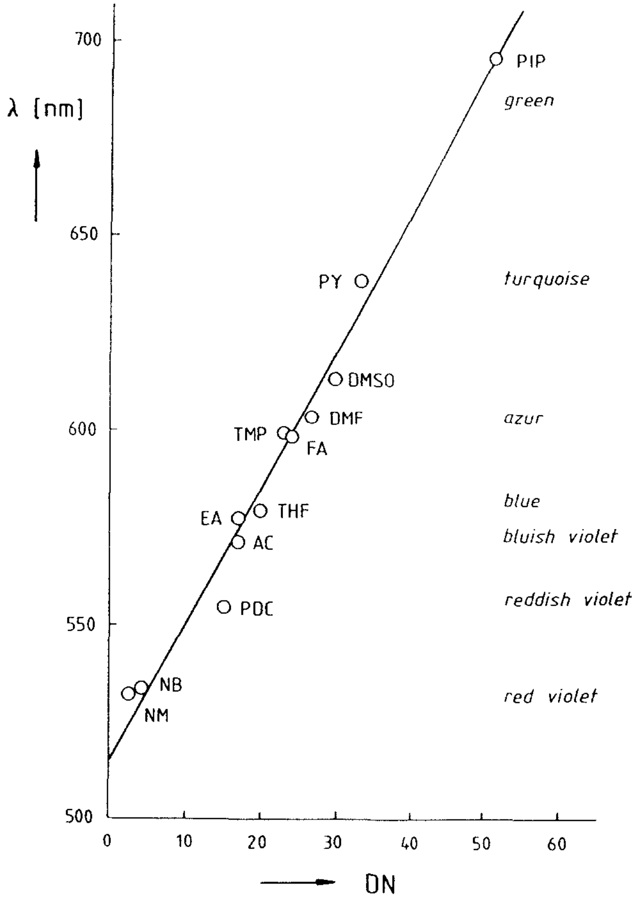


Fig. 13. Changes of wavelength of the charge transfer bands Cu(tmen)(acac)$B\phi_4$ in solvents of different donor number (DN) [36].

two distinct species. Because of the exothermicity of this reaction, thermochromism is also found, especially for donor solvents of intermediate donor strength.

$$[\mathrm{Ni}(\beta\text{-dike})(\mathrm{diam})]^{+} + 2\mathrm{D} \rightleftarrows [\mathrm{Ni}(\beta\text{-dike})(\mathrm{diam})\mathrm{D}_2]^{+}$$

square planar	octahedral
diamagnetic	paramagnetic
red	blue or green
Ni – O bonds shorter	Ni – O bonds longer
C = O bonds longer	C = O bonds shorter
C – C – bonds shorter	C – C – bonds longer

Electron-withdrawing substituents at the β-diketone lead to lengthening of the M—O bonds associated with increase in stability constant of the octahedral species, whereas electron-releasing substituents at the β-diketone lead to shortening of the M—O and M—N bonds and to a decrease in the stability constant. Change of substituents at the diamines lead to changes in the symmetry of the octahedral complexes and to decreasing equilibrium constants in the order of increasing size of the substituents. In both the copper and the nickel complexes, the M—O as well as the M—N bonds are lengthened by coordination of the donor ligands. Likewise, the C=O bonds of the β-diketone are lengthened, whereas the neighbouring C—C— bonds are shortened (see Fig. 14).

These effects are less pronounced at the respective C—N bonds and the C—C bonds in the diamine. It is interesting to note that electron-releasing substituents at the diamine have the same effect as electron-withdrawing substituent at the β-diketonate. The latter have a more decisive influence than the former (Fig. 15). The resulting changes in electron distribution, in bond length and in bond angles are the same as those resulting from the donor influences of the donor solvent. This is found for both the five- and the six-coordinate species and explains why the stability constants of both the five- and the six-coordinate species are drastically increased by electron-withdrawing substituents. These effects are also reflected in the IR and far-IR absorption frequencies [41]. The charge redistribution depends upon the donor strength of the solvent donor molecule, D, and leads, in the case of the less symmetrical five-coordinates species, to considerable changes in the bond angles (see Fig. 15).

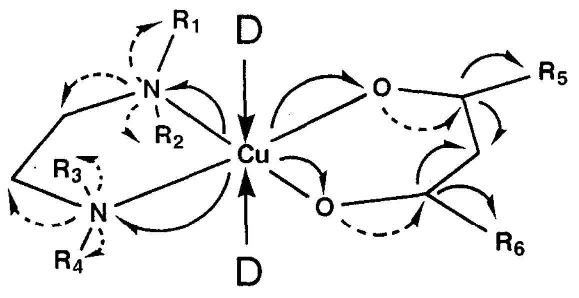


Fig. 14. Scheme of electron redistribution and bond length variation in Cu(tmen)(acac)BF_4 induced by interaction of the coordination centre with donor solvent molecules, D.

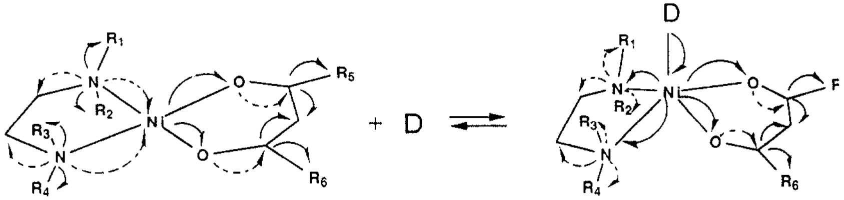


Fig. 15. Influence of electron-withdrawing substituents (e.g. $-CF_3$) at the β-diamine and electron-releasing substituents (e.g. $-CH_3$) at the diamine ligand upon the electron distribution, the bond length and the bond angle for the square planar and the five-coordinate species. Left-hand side: arrows denote substituent effects; right-hand side: arrows denote the donor effects.

As in trimethylchlorostannane, these changes are reflected in the ratios of the intensities of symmetrical and asymmetrical molecular vibrations in the far-IR spectra and have been interpreted by change in mechanism in the course of the formation of the octahedrally coordinated nickel-complex. Actually, a five-coordinate intermediate appears in both the nickel and copper cases [40]. Analysis of the temperature-dependent equilibrium constants revealed two isokinetic groups, namely one for solvents of medium donor number, such as acetonitrile, acetone, alcohols, etc., and another for strong donor solvents, such as formamide, *N*,*N*-dimethylformamide, pyridine, dimethylsulphoxide, etc. According to the bond angle variation rule, strong donor solvents provoke a strong distortion of the planar arrangement of the β-diketonate and the diamine in the five-coordinate species. At the same time, the Ni—O bonds at the β-diketonate are weakened. Thus, in strong donor molecules, one Ni—O bond is broken, the β-diketonate rotates and a cis configuration results. In weak donor solvents these changes are less pronounced, so that the β-diketonate remains in nearly the same position within the molecule and the second donor molecule is simply added to form the trans isomer. The former reaction path may be described in terms of a dissociative mechanism and the latter in terms of an associative mechanism.

The decrease in electron density at the electron-releasing substituent of one ligand leads to an increase in electron density at the electron-withdrawing substituent of the other ligand, whereas the electron density near the coordination centre remains nearly invariant.

(iii) Solvent effects on hexathiocyanatochromate(III)

Solvatochromism is also observed for the hexathiocyanatochromate(III) ion [42,43]. The two absorption bands in the UV–visible spectra of this compound show large solvent dependence in their molar absorbancies. Increasing donor properties of the solvent also shift the band positions, despite the fact that outer sphere interactions occur [43,44].

Due to coordination of solvent molecules to the NCS^- groups [45], the C—S bond seems to be significantly weakened in agreement with the bond length variation rules [46], whereas changes of bond length of the Cr—N and the N—C bonds are hardly detectable. MNDO results [43] show a linear correlation of calculated atomic charges with the donor number, and the effect is greatest at the sulphur atom. It is surprising to see the sulphur atom acting as an acceptor towards the solvent, but this is concluded from the dependence on the donor rather than on the acceptor properties of the solvent and from the MNDO calculations showing an overall transfer of charge from the solvent. This is also reflected in the dependence of reduction potentials upon the donor properties. The negative charge at the NCS^- nitrogen atoms seem to be decreased with increasing donor number of the solvent. The overall effect is therefore an increasing polarization of the NCS^- ligands with increasing donor properties of the solvent. These observations may be described in terms of a σ attack at the sulphur atom and a π back-donation through the Cr—N=C=S π-system, yielding a decrease in electron density at the chromium atom and an increase in electron density at the sulphur atom with the N—C bond acting as a π-bridge. The MNDO calculations support this view.

I. MOLECULAR SYSTEM ORGANIZATION: CHEMICAL FUNCTIONALITY

In order to make observations and to obtain reproducible results, any investigated system must have an “ability” to react specifically towards changes in the environment whereby its main characteristics and functionalities are maintained [47]. Eigen and Winkler [48] referred to molecules with particularly well-developed abilities to maintain their integral configuration and functionality under different conditions as “intelligent molecules”. In this way, they expressed the fact that the properties of the molecules are partly subject to the conditions of the environment and that knowledge of structure and properties of “single” molecules is not sufficient to account for their actual behaviour. Such a behaviour implies a “system organization”, which enables them to respond to changes in the environment either by developing forces against those acting on the system or to “escape” such forces.

The concept of “chemical functionality” has been developed as a first step on the way to extend the donor–acceptor concept to all types of chemical interactions [49] and is based on the distinction between redox reactions and acid–base reactions (in the widest sense) and their idealistic descriptions as transfer of electrons (electron donor (ED)–electron acceptor (EA) interactions) and as sharing of electron pairs (electron pair donor (EPD)–electron pair acceptor (EPA) interactions), respectively. Because, due to an electron transfer (redox reaction) the actual changes in net charges are found to be smaller than the charges of the electrons transferred, it is assumed that, within the developing species, an acid–base-type interaction (electron pair donor–electron pair acceptor) is induced to compensate (at least in part) the effect of the redox (electron donor–electron acceptor) interaction. In the course of the redox reaction

$$\underset{\text{ED}}{[\text{Fe}(\text{OH}_2)_6]^{2+}} \rightleftharpoons \underset{\text{EA}}{[\text{Fe}(\text{OH}_2)_6]^{3+}} + \text{e}^-$$

Fe(II) acts as an ED, but the loss of an electron is partly compensated by an induced increase in EPA property at the coordination centre and hence the strengthening of the solvate bonds: the ED function of Fe(II) is followed by the EPA function of Fe(III), so that the change in net charge at the iron nucleus is less than one. In the Fe(phen)_3 complexes, the ED effect is even slightly overcompensated by the EPA effect.

In an analogous manner, the ionization of a covalent bond is described in terms of EPD–EPA interactions followed by an internal charge transfer without which the ionization would remain unexplained. For example, the ionization of LiCH_3 in ether involves EPD interactions of ether molecules with the lithium site acting as EPA. As the positive net charge of the latter is decreased, it acts as a kind of ED towards the methyl group with formation of the charged particles to give [49]

$$\underset{\text{EPD}}{n\text{R}_2\text{O}} \rightarrow \overset{\text{e}^-}{\overbrace{\underset{\text{EA}}{\underset{\text{EPA}}{\text{Li}}} - \underset{\text{ED}}{\text{CH}_3}}} \rightleftharpoons (\text{R}_2\text{O})_n\text{Li}^+ + \text{CH}_3^-$$

The ionization of HCl in water is due to the EPA function of the hydrogen atoms of HCl and to the EPD functions of the chlorine atom towards water molecules. Consequently, an ED function at the hydrogen atom and an EA function at the chlorine atom develop in order to achieve ionization [49].

$$\underset{\text{EPD}}{n\text{H}_2\text{O}} \rightrightarrows \overset{\text{e}^-}{\overbrace{\underset{\text{ED}}{\underset{\text{EPA}}{\overset{\delta+}{\text{H}}}} - \underset{\text{EA}}{\underset{\text{EPD}}{\overset{\delta-}{\text{Cl}}}}}} \leftleftarrows \underset{\text{EPA}}{m\text{HOH}} \rightleftharpoons \text{H}(\text{OH}_2)_n^+ + \text{Cl}(\text{HOH})_m^-$$

In these ways those aspects of a molecular system organization [47] have been formulated which concern the "abilities" of the molecules to compensate changes in electron redistribution. Such behaviour would be impossible unless the different parts of the whole system are in continuous cooperation or, as Weiss [50] said: "a unit retains its unity by virtue of the power of subordination, which it exerts on the constituent elements in such a manner that their individual activities are directed towards a combined unitary resultant." The introduction of artificially "hierachic levels" has been suggested. These are necessary in order to obtain a simplified division of the actual differentiation into more clearly arranged categories [51, 52]. The various hierarchic levels are chosen in such a way as to express certain differences in dominance between them and to provide an orientation for further questions, but it must be kept in mind that a hierarchic level is always an integral part within the system and it cannot be considered as a separate entity. Because it cannot be within the scope of this article to provide a review on molecular system organization [24,51–54], the conclusions may simply be stated.

(i) System organization in iron–phenanthroline complexes

The greatest invariance to electronic changes, caused, for example, by redox reactions, substitution and solvent effects, is displayed by the charge density region around the coordination centre [24]. It appears to act as a kind of "regulating centre", and it is considered as the highest accessible hierarchic level. Its "inertia" seems to be due to its outstanding ability to redistribute electronic charges over the whole complex unit, which is thereby reorganized. Immediately subordinate to this level appear the peripheral regions of the ligands, which are essential for communication with the environment. Changes in electronic charges of the whole unit are most pronounced in the molecular boundary areas, i.e. the increase in positive charge due to oxidation to the Fe(III) complex are distributed over all of the peripheral hydrogen atoms, which are increased in positive net charge accordingly. The occurrence of six reversible polarographic reduction waves of tris(4,7-diphenyl-phenanthroline)iron(II) is due to the fact that the increasing electronic charges are distributed over all the outer regions of the ligands [55]. The π-electron systems, which fulfil buffer functions between the regulating centre and the boundary areas, appear to be subordinated to this level. According to circumstances, they are capable of executing either donor or acceptor functions towards other regions. In these ways, the π-electron system helps to maintain the basic structural framework of the system with the areas of σ-bonds, which is considered as the lowest hierarchic level.

These considerations suggest that (a) the static features of the lowest hierarchic level are maintained dynamically under the auspices of the higher levels and (b) they provide, at the same time, the static framework for the execution of the better developed dynamic actions of the higher levels. It is therefore important to realize that each of the hierarchic levels is important for the organization and hence for the existence of the system under consideration. As the external conditions are changed, the highest level will "decide" in which ways the other levels will be reorganized in order to respond properly through their concerted actions for the maintenance of the chief characteristics of the system. The higher levels are dynamically more active and more resistant towards changes; the lowest levels are more rigid and more passive. Their mutual interactions may be illustrated by considering a river. Its bed and embankment are slightly, but continuously altered, even if the speed and the quantity of the flowing water remains nearly constant, although it is altered increasingly as the rate of flow is increased. With a reduction of the quantity of flowing water, the river will be silted up, while an increase may cause the river to overflow, the bed to deepen and the banks to change their shape. In other words, any change in the rate of flow (dynamic features) causes changes in river bed (static boundary conditions) and these in turn have an influence on the dynamic aspects.

Unfortunately, it is not possible to gain complete knowledge about the enormous varieties and possible differentiations within the charge density pattern and hence of the molecular system organization. Their considerations appear, however, to be of great value for scientific investigations, in particular in biochemistry and biology, and this may be briefly illustrated for haemoglobin.

(ii) Molecular system organization of haemoglobin

The unique properties of haemoglobin in the red blood cells suggest a highly developed system organization. It responds in highly specific ways to changes in environment. It serves highly specific purposes [51], namely to carry oxygen from the lungs to the tissues and to provide appropriate conditions in its surrounding cell plasma for the transport of carbon dioxide from the tissues to the lungs and to assist its release.

A haemoglobin molecule is made up of four polypeptide chains, two of them containing 141 amino acid residues and two of them 146 amino acid residues each. Each chain harbours one haeme group which gives blood its red colour and which is a flat porphyrin ring with an iron atom sticking out of its centre [56,57]. Each haeme group is connected to the protein by means of a histidine group, which provides the principal path for communication between the haeme and the rest of the molecule. As soon as one of the four iron atoms has taken up oxygen, the other follow immediately and the same is true for the release of oxygen. Each haeme group is enfolded in a polypeptide chain lying deeply in a pocket of the molecule.

When oxygen is coordinated to an iron atom, the O=O bond is somewhat lengthened ("back donation"). Each of the iron atoms is pushed into the porphyrin ring and transition takes place from the high-spin to the low-spin complex. The latter phenomenon shows that the molecule is more rigid when transporting oxygen (low-spin state). In the course of the transition, the whole system passes a state of maximum specific heat associated with a highly dynamic state (i.e. a high system organization [25,58]) as already described for spin-transition systems. The great flexibility is reflected in the enormous conformational change that results either from coordination or from the release of oxygen. It is important to note that, for every four molecules of oxygen taken up, two protons are released from the terminal positions of the protein chains into the cell plasma to release CO_2 from the HCO_3^- ion and that for every four molecules of oxygen released, two protons are attached to these chains in order to bind CO_2 in the aqueous phase of the plasma.

As all of these effects disappear as soon as the haemoglobin molecule is split in half, the whole molecule must act as a particularly well-organized unit. The high development of the molecular system organization is also seen from the ability to fulfil all of these actions almost irrespective of temperature within the range 35–42°C, which is associated with a highly developed supermolecular system organization of the aqueous phase [59,60].

In the haemoglobin molecule, the highest hierarchic level seems to be provided by the charge density around the iron atoms. All conformational changes, as well as the regulation of the pH value within the environmental cell plasma, appear to be regulated by the interactions between the iron atoms of the haeme groups and oxygen molecules. Because the peripheral groups are changed in such ways as to allow the transportation of carbon dioxide, as regulated by the highest level, the peripheral electron areas appear to be subordinated to the former. All other parts of the molecule seem to be subordinated in different ways and each of them has specific functions and none can be omitted. This can be seen from the inability of haemoglobin-S to transport oxygen, although it differs from haemoglobin in only one amino acid position. If haemoglobin is replaced by haemoglobin S in the erythrocyte, even the shape of the latter is changed.

(iii) Conclusion

In accordance with quantum mechanics, changes in bond lengths and bond angles due to changes in molecular environment are well understood. The new approach to investigate molecular system organizations is not meant to provide more precise quantitative evaluation, but rather to provide a better understanding for the changes in qualities.

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