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# The Principle of Hard and Soft Acids and Bases and the Problem of Competitive Coordination in Complex Compounds

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A systematic and general account is given of data on the location of the coordinate bond in systems with several potential electron-donating centres (competitive coordination). The problem is examined from the standpoint of the principle of hard and soft acids and bases.
The biliography includes 441 references.

CONTENTS

I. Introduction 341
II. The fundamental concepts of the principle of hard and soft acids and bases 341
III. The location of the coordinate bond in systems with several electron-donating centres: competitive coordination 342

## I. INTRODUCTION

The principle of hard and soft acids and bases (HSAB), put forward by Pearson[1] in 1963 has been recently widely adopted in chemistry not only as a result of the author's own efforts[2-6] but also due to the publication of monographs[5,7-9], reviews[10-16], and original papers[17-25] in which certain problems of inorganic, organic, and coordination chemistry as well as the chemistry of organic derivatives of the elements have been discussed from the standpoint of hard and soft acids and bases.

The HSAB principle is based on three fundamental postulates: (I) the majority of chemical reactions may be regarded as of the acid–base type[1-6] and compounds can be treated as complexes of Lewis acids and bases[4]; (2) all acids (A) and bases (B) can be classified as hard (H), soft (S), and intermediate (I);[1-6,11] (3) acid–base reactions take place in such a way that hard acids (HA) are preferentially coordinated to hard bases (HB) and soft acids (SA) are preferentially coordinated to soft bases (SB).[1,4,5] The reactivities of the intermediate acids (IA) and bases (IB) require a specific consideration.

The above postulates, combined in the HSAB principle, are not new to chemists, since (1) the possibility of assigning chemical reactions to the acid–base category follows directly from the Usanovich theory[26], as rightly pointed out by Yatsimirskii[13], Day and Selbin[27], Evans[18], and Denes[28]; (2) the classification of acids which follows from the HSAB principle is identical with the classification of metal ions into classes A and B (Schwarzenbach[29]) or a and b (Ahrland, Chatt, and Davies[30]), as was emphasised by Pearson himself[4,5] and also in monographs[31,32] and reviews[10,33]; an approach to the estimation of softness and hardness of bases was suggested by Schwarzenbach[34,35]; (3) the preferential coordination of hard acids to hard bases and of soft acids to soft bases has long been known to chemists as the postulate of the predominance of electrostatic or covalent interaction in individual acid–base reactions (including donor–acceptor reactions[13]). This fact, which follows from classical polarisation concepts of coordination chemistry, has been pointed out in monographs[36-38] and original papers[13,39]. Here it is interesting to note that in his paper published in 1962, Hudson[40] states directly that polarisable ions tend to react at polarising centres, while non-polarisable ions react at charged non-polarising centres".

Nevertheless, these postulates, which are familiar and comprehensible to chemists and which have been tested on numerous examples[1-25,30-38,41], have been frequently disregarded and have not yet been considered in the discussion of many general and specific problems of organic, inorganic, and coordination chemistry as well as in the chemistry of organometallic compounds.

In this connection the undoubted usefulness of the HSAB principle in individual correlations and the general correlation of a large number of experimental facts concerning primarily the stability and reactivity of inorganic, organic, and coordination compounds and organometallic compounds must be recognised. This is confirmed by the finding that the formulation of the HSAB principle[1,2] and its vigorous propagation[3-7] stimulated the consideration of problems of the stability of coordination[5-7,13] and organic[4,6,14-16] compounds and their reactivity[4,8,14,17,24], the problem of electronegativity[18,19], and also the consideration of the nature of the attacking agent in quantum-chemical estimations of reactivity[20].

In the present review an attempt is made to apply the HSAB principle in the discussion of the problem of the location of the coordinate bond in the chemistry of coordination compounds. The enormous amount of experimental data accumulated on this problem has already been the subject of some discussion[7,12,24,25,33,42], but this has been unduly narrow[12,42] or insufficiently objective[33].

Among the very large amount of data published on this question, we have considered mainly those of the last five years.

## II. THE FUNDAMENTAL CONCEPTS OF THE PRINCIPLE OF HARD AND SOFT ACIDS AND BASES

Using the criteria of hardness and softness, Pearson compiled Tables classifying acids and bases[1-6]. Despite the wide range of acids and bases covered and the satisfactory treatment of the preferred paths for reactions, Pearson's classification is in many ways arbitrary and in many cases cannot be used to account for the reactivity of coordination and organic compounds as well as organic derivatives of the elements.

The stability series of complexes with electron-donating atoms found on the basis of the existing classifications[4,29,30]:

$$\text{hard}\begin{cases}N \gg P > As > Sb\\ O \gg S > Se > Te\\ F \gg Cl > Br > I\end{cases}\qquad \text{and soft}\begin{cases}N \ll P < As < Sb\\ O \ll S \sim Se \sim Te\\ F < Cl < Br < I\end{cases}$$

are valid only when one disregards electronic and steric factors in molecules[14], which may alter significantly the "softness" and "hardness" of both an acid and a base. This has been frequently pointed out[7,10,31,32] in the assessment of the stability series of complexes using the classification of Ahrland, Chatt, and Davies[30]; these remarks are undoubtedly valid also for Pearson's classification Tables. When estimating "hardness" and "softness" of acids and bases, it is particularly important to take into account electronic and symbiotic effects[4,7,43], which may result in the "transfer" of an acid or base, particularly those of intermediate types, from one category to another (SA–IA–HA or SB–IB–AB). Numerous data useful in understanding the arbitrary nature of this type of classification in organic chemistry are given in a paper by Nesmeyanov and Kabachnik[41], in the reviews of Gompper[44] and Shevelev[14], and in Sokolov's papers[24,45] or organic derivatives of the elements.

In estimations of "hardness" and "softness", an important role must be attributed to specific reaction conditions and the effect of the solvent[4,14,40]. We believe that in this respect the "hardness" of the proton and "softness" of the methyl cation ($CH_3^+$) are particularly instructive. The entire data quoted by Pearson[4] appear to be consistent with his conclusion that the methyl cation is "softer" than the proton. However, data on the affinities of the proton and the methyl cation for various bases in the gas phase suggest that they are equally "hard".[13]

Thus Pearson's classification as well as earlier classifications (Chatt, Schwarzenbach)[29,30] are very approximate and should be used with a certain amount of caution.

Classifications of acids and bases according to Yatsimirskii[13].

| No. | Groups | Acids | Bases |
|---|---|---|---|
| 1 | Ionic | $Cs^+$, $Rb^+$, $NH_4^+$ | $BR_4^-$ |
| 2 | $\sigma$-Acceptor acids, $\sigma$-donor bases | $H^+$, $CH_3^+$, $CR_3^+$, $BR_3$ | $H^-$, $CH_3^-$, $NR_3$, $NH_3$ |
| 3 | Strong $\sigma$-acceptors and donors; weak $\pi$-acceptors and donors | $Li^+$, $Be^{2+}$, $Mg^{2+}$, $Al^{3+}$ $Sc^{3+}$, $Zr^{4+}$, $Hf^{4+}$ | $OH^-$, $H_2O$, $OR^-$ $RCOO^-$, $XO_n^{2-}$, $F^-$ |
| 4 | Strong $\sigma$, $\pi$-acceptors; strong $\sigma$, $\pi$-donors | $Tl^+$, $Pb^{2+}$, $Sn^{2+}$, $Bi^{3+}$ $Ga^{3+}$, $In^{3+}$, $Tl^{3+}$ | $Cl^-$, $Br^-$, $S^{2-}$ $RS^-$, $R_2S$ |
| 5 | $\pi$-Acceptors; $\pi$-donors | $Fe^{n+}$, $Co^{n+}$, $Ni^{2+}$, $Cu^{n+}$ $Ag^+$, $Cd^{2+}$, $Pt^{II}$, $Pd^{2+}$ | — |
| 6 | $\pi$-Donors; $\pi$-acceptors | — | CO, $CN^-$, $C_5H_5^-$ $CNS^-$, $R_3P$ |

In this connection Yatsimirskii's classification, based on the assignment of acids and bases to different categories on the basis of the types of bonds formed by them, appears to be more correct[13].

Not being in a position to characterise in detail each of the groups quoted in the Table, we shall point out that groups 2 and 3 are hard (group 1 belongs to the category of acid–base reactions with electrostatic interaction[13,26]) and groups 4–6 combine soft acids and bases.

We see the advantages of Yatsimirskii's classification not only because of a more rigorous approach to the nature of acid–base interaction in its derivation but also because of the more correct distribution of cations and anions among different classes which follows from it. These considerations concern primarily the $H^+$, $CH_3^+$, and $CR_3^+$ hard cations which belong to one group, and the separate assignment of $Al^{3+}$ and $Sc^{3+}$ to hard cations (group 3) and of $Ga^{3+}$ and $In^{3+}$ to soft cations (group 4). It is shown below that in most cases the classification of all the cations included in group 5 as soft is justified. At the same time the assignment of quadrivalent zirconium and hafnium to hard cations (group 3) is not always justified and in this case account must be taken of the symbiotic effects of anions[4,7,43].

A quantum-chemical basis has been obtained for the HSAB principle[5,46,47] using the mathematical apparatus of the simple perturbation theory[48]. This approach is unduly narrow and suffers from many disadvantages[20,49]. However, such discussion is outside the scope of the present review.

## III. THE LOCATION OF THE COORDINATE BOND IN SYSTEMS WITH SEVERAL ELECTRON-DONATING CENTRES: COMPETITIVE COORDINATION

In the discussion of the problem of competitive coordination, one must distinguish non-conjugated and conjugated systems. The first type includes saturated compounds (or compounds with isolated multiple bonds) where the reaction centres are separated from one another by at least one atom with a saturated valence. In compounds of the second type, the electron-donating centres are linked in a single mesomeric system (ambident compounds[50])†. From the theoretical standpoint, such division is based on the important difference between localised and delocalised orbitals.

### 1. Experimental Methods for Solving the Problem of Competitive Coordination

X-Ray diffraction analysis constitutes a direct and reliable method for the determination of the site where the coordinate bond is located and the complete elucidation of the structure of complexes. It has been frequently used to unravel molecular structures with different potential electron-donating centres: complexes of pseudohalides (NCX; X = O, S or Se),[12,51,52] urea,[33,53] thiourea,[54–56] dimethyl sulphoxide[57], morpholine[58], thiocarbazide[59,60], thioacetamide[61], and many other complexes[10,33]. However, the scope of X-ray diffraction analysis is limited owing to the amount of labour involved.

Most studies in this field have used spectroscopic methods, among which vibration spectroscopy has the greatest importance[62–74]. Its scope in coordination chemistry has been quite fully discussed in well known monographs[9,38,42,68,69] and therefore does not require special consideration. We shall only mention that, when infrared spectroscopy is employed, one must use considerable caution in those cases where the displacements of

†In their review, Norbury and Sinha[33] did not always consider the necessity for the conjugation of reaction centres in the definition of ambident ligands. Therefore, among the ambident compounds they consider, there are also non-conjugated systems, for example 1,4-oxathiane.

many ligand vibration frequencies during coordination interaction are used to draw conclusions as to the location of the bonds. The most accurate of such information has been obtained from calculations of molecular infrared spectroscopic data [69,70]. We believe that low-frequency infrared spectroscopy [71-74], whereby it is possible to determine directly the type of M–X bonds (X is an electron-donating atom), is promising in the study of the type of coordination [73].

Among other methods, mention should be made of electronic spectroscopy. Comparison of the theoretically predicted behaviour of a ligand in coordination to different electron-donating atoms with the experimental spectrum yields reliable evidence on the location of the bond. An instructive series of such studies have been carried out [75-79]. Other methods for using electronic spectroscopic data in the solution of the problem of competitive coordination are also known [33,78].

On further development of NMR spectroscopy, this method too will find wide application in this field of coordination chemistry. However, so far its use is limited (see for example, Refs. 17, 62, 63, 71).

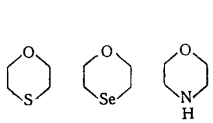
Modern quantum-chemical methods yield definite quantitative values for the electron distribution in molecules and therefore may be used to predict the direction of attack in systems with several electron-donating centres. Although so far few studies involving quantum-chemical calculations have been made in this field [12,52,80-84], they suggest that the coordinate bond is usually located at the electron-donating atom with the highest negative $\pi$-electron density.

In conclusion we may note that best results may be obtained by employing a combination of methods‡, including synthetic methods [75,80].

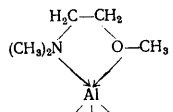
## 2. Non-conjugated Systems

The available literature data show that the location of the coordinate bond in non-conjugated systems in general obeys the requirements of the HSAB principle when account is taken of the hybrid state of the electron-donating atoms and of steric factors.

1,4-Oxathiane (I) and its selenium analogue (II) are perhaps the most successful models for the consideration of competitive coordination from the standpoint of the HSAB principle:




(I) (II) (III)




(IV)

Compounds (I) and (II) contain atoms, isolated from one another, belonging to the same group of the Periodic System, so that, according to the HSAB principle, in their interaction with hard acids, the coordinate bond should be preferentially located at the oxygen atom (hard centre) and in the interaction with soft acids, at the sulphur [compound (I)] or selenium [compound (II)] atom (soft electron-donating atoms). Experiments have confirmed these considerations.

‡The application of Mössbauer spectroscopy in this field is also promising [64,85].

The possibility of different sites of location of the coordinate bond (at oxygen or sulphur atoms) involving oxathiane was first formulated by Hendra and Powell [86], who established that in complexes with $CuCl_2$, $HgCl_2$, and $PtCl_2$, 1,4-oxathiane behaves as a monodentate ligand (only one of the electron-donating atoms is involved in coordination interaction). Subsequently it was shown in a series of studies [17,87-93] that the hard acids $AlX_3$ (X = Cl or Br)§ and $BF_3$ combine with the hard nucleophilic centre (oxygen) while the softer transition metal halides in the highest state of oxidation¶ combine with the soft sulphur and selenium atoms.

Platinum, palladium, rhodium [93], and mercury [92,94] salts also combine with the sulphur atom of compound (I). The above studies were carried out mainly by infrared and NMR spectroscopic methods [62,87-93] and the reliability of the conclusions may be open to certain objections because the vibration frequencies of the C–X–C linkages (X = O, S, or Se), on whose behaviour in coordination interactions the principle conclusions are based, are relatively non-characteristic. The work of McEwen and Sinn [94], where the coordination of mercury and sulphur atoms was demonstrated by an X-ray diffraction study of the $HgCl_2.I_2$ complex, is superior in this respect.

Morpholine (III) contains identically hybridised oxygen and nitrogen atoms, the first of which, being more electronegative [95], is therefore harder than amino-nitrogen. In this case too the location of the coordinate bond agrees with conclusions based on the HSAB theory: soft (AgI) [58] and intermediate (salts of many bivalent [96,97] and tervalent [98] metals) acids combine with the nitrogen atom. Only in the case of $Al(CH_3)_3$ is it possible to obtain a complex with the composition $2Al(CH_3)_3$.(III) where both centres are involved in the coordination interaction [99]. Probably the coordinate bond involves the oxygen atom also in the platinum complexes of morpholine [100]. Identically hybridised oxygen and nitrogen atoms are present also in $\alpha$-dimethylamino-$\beta$-methoxyethane which forms a cyclic structure (IV) with $Al(CH_3)_3$. [101] However, in this case it is difficult to assess the competitive interaction of oxygen and nitrogen atoms owing to both the limited selection of acceptors and to the energy gain usually observed on formation of cyclic structures of type (IV). The latter factor must be always considered in the study of the competitive coordination of ligands the electron donating centres of which may be involved in the formation of metal-containing rings.

This approach appears to be particularly useful in studies of the possibility of the coordination of acids and their esters. These compounds are convenient models for a comparison of the coordination capacities of the $sp^3$-hybridised nitrogen atom (amino-group) and the oxygen atom (amino-group) and the oxygen atom in the $sp^2$-hybrid state (the carbonyl group). On the basis of the foregoing considerations, amino-nitrogen may be regarded as a softer electron-donating centre than the carbonyl oxygen.

§In the review of Norbury and Sinha [33], the halides $AlX_3$ are erroneously included in the group of acids combining with the sulphur atom of oxathiane.

¶The softness of cations of this kind is associated not only with the highest degree of oxidation of the metal but also with the symbiotic effect of the X anion. In particular $TiCl_4$ forms more stable complexes with dialkyl sulphides than with ethers [88], i.e. is a soft acid according to the HSAB classification.

This idea is confirmed by the finding that in complexes of $\alpha$- and $\gamma$-amino-acids (AH) of the type $[(AH)_2Pt(NH_3)_2]Cl_2$ as well as in the glycine complexes $(GlH)-Pt(GlH)_2Cl_2$, the soft acid $PtCl_2$ is linked to the amino-nitrogen [102,103]. Similarly $\alpha$-aminoacid esters may react with salts of comparatively soft bivalent metals as monodentate ligands with preferential formation of an M–N bond (only with methyl-L-tryptophan is coordination involving the C=O group observed) [104]. However, in most cases [105–107] amino-acids behave as bidentate ligands and form cyclic chelate compounds.

Similar cyclic structures arise in the coordination interaction of thio- and seleno-semicarbazides [108,109] with metal salts, although there is evidence that comparatively soft acids combine preferentially with the softer sulphur and selenium atoms [110,111]†.

Aminonitriles with the general formula $R_2N(CH_2)_nCN$ have two electron-donating centres: $sp^3$- and $sp$-hybridised nitrogen atoms. If one bears in mind that the electronegativity, which in many ways determines the hardness of nucleophilic agents [4], increases with the amount of s-character in the hybrid orbitals of the nitrogen atoms [95,112], one must assume that the nitrogen atom of the nitrile group is a harder donor than the amino-nitrogen. Therefore, in agreement with the HSAB principle, only may assume that hard acids will combine preferentially with the hard nitrile nitrogen and soft acids with the amino-nitrogen. Experimental data agree with these considerations. In the case of hard $BCl_3$, an increase of the vibration frequencies of the nitrile group in the aminonitrile with $R = C_2H_5$ and $n = 1$ is observed [113], showing that the coordinate bond involves the nitrile nitrogen [114–116]. The comparatively soft $MX_4$ (M = Sn, Ti, or Zr; X = Cl or Br) form complexes without involving the nitrile group [113]. However, with $n = 2$ or 3, the $MX_4$ also form cyclic structures and both electron-donating nitrogen atoms of the aminonitrile are involved in the coordination interaction [112].

Not only individual atoms but also the $\pi$ bonds of unsaturated hydrocarbons can behave as soft electron-donating centres. Electron-donating systems of this kind include allylamines [117–120] and aminoallene and aminoacetylene hydrocarbons [121].

Depending on the reaction conditions, allylamine can behave as a monodentate or a bidentate ligand. As expected, in the first case $PtCl_2$ combines with the $\pi$ bond of the ethylene group [119], which is a softer centre, and in the second case it combines with both electron-donating centres, forming dimeric bridge structures [117,118] or monomeric cyclic structures [119,120]. The latter are characteristic also of complexes of bivalent nickel, cobalt, manganese, copper, iron, zinc, and cadmium and tervalent iron, chromium, cerium, and praseodymium with aminoallene, aminoethylene, and aminoacetylene ligands [121].

### 3. Systems with Conjugated Bonds (Ambident Ligands)

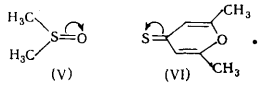
Examination of competitive coordination in compounds with conjugated electron-donating centres is very important not only because of the great range (mentioned above) of the reactivities of ambident systems but also because it deals with the salt [122] or structural [123] isomerism, which is extremely important for coordination symmetry‡.

From the standpoint of the HSAB principle, the problem of the location of the coordinate bond in conjugated systems with several electron-donating centres is of special interest, since nucleophilic atoms in ambident compounds become harder or softer, mainly under the influence of electronic effects, than in the isolated ligands or in the non-conjugated systems discussed above.

#### a. Ambident Ligands with Electron-donating Atoms of Elements in the Same Periodic Group

Oxygen and sulphur (selenium) atoms. In conjugated systems containing the hard oxygen atoms and the soft sulphur and selenium atoms, the position of the coordinate bond is generally consistent with the requirements of the HSAB concept: typical [1,25] soft acids (Pt, Pd, Rh, Hg) form a bond with the sulphur and selenium atoms, while harder acids (Al, Th) combine with the oxygen atom [10,33]. However, with intermediate acids (salts of bivalent metals, metal carbonyls), the oxygen atom is preferentially involved in the formation of the coordinate bond [33], although a bond with the sulphur atom is also observed. Thus not only iridium [126,127], palladium [128], platinum [129], and rhodium [130], but also cobalt [28,131] forms bonds with the sulphur atom of the sulphite anion. A bond with the sulphur atom is formed by the majority of metals [33,132,133] and their carbonyls [134] in complexes with sulphur dioxide and also sulphones and sulphonyl chlorides [33]. On the other hand, the hard $AlCl_3$ forms with the ligands of the last type complexes involving Al–O bonds [135].

There is a particularly large amount of data concerning the location of the coordinate bond in sulphoxide complexes. Intermediate and hard cations [10,28,136–143], organometallic derivatives [144–147], and even metal carbonyls [148] combine with the oxygen atom of dimethyl sulphoxide (DMSO) (V). However, in accordance with the HSAB principle, soft acids are coordinated via the sulphur atom [33,149–156]. The conclusions reached concerning the mode of coordination of DMSO give rise to no doubts not only owing to the reliability of the assignment of the S=O frequencies [68] but also because the conclusions were in many cases based on X-ray diffraction data [144,157–159]. Complexes with M–O bonds only have been described for dimethyl selenoxide [10,33]:



(V) (VI)

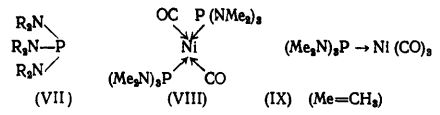
The different coordination behaviour of sulphoxides (compared with oxathiane and oxaselenane discussed in the preceding section) can probably be accounted for by a mesomeric effect which increases the "softness" of the oxygen atom. A similar effect may be observed for the sulphur atom in 2,6-dimethyl-4-thiopyrone (VI), for which M–S bonds have been described [160].

Nitrogen and phosphorus atoms. Tri-(*NN*-dialkylamino)phosphines (VII)—ambident systems containing tervalent electron-donating nitrogen and phosphorus

†It was stated in this study that the mode of coordination of thiosemicarbazide depends on the assignment of the metals to the Chatt classes a and b.

‡Recently this type of isomerism has been referred to as linkage isomerism in non-Soviet literature [5,124]; in Soviet coordination chemistry this concept is given a different significance [125].

atoms—are extremely sensitive to the "hardness" and "softness" of acids:



(VII) (VIII) (IX) (Me=CH$_3$)

The soft $HgI_2$, $CdI_2$,[161] and $BH_3$ [162,163] form adducts with aminophosphines which involve an M–P bond, while the harder $BR_3$, $BCl_3$, $BF_3$,[163] and $PCl_3$ [164] attack the nitrogen atom and dissociate the P–N bond:

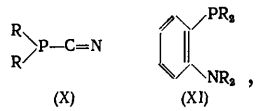
$$(NMe_2)_3P \rightarrow BH_3 \xleftarrow{(BH_3)_2} P(NMe_2)_3 \xrightarrow{BX_3(X=F,Cl)} Me_2NBX_2 + PX_3 .$$

Molecular complexes involving the "soft" phosphorus atom are also formed[161] when aminophosphines react with $Ni(CO_4)$ (VIII, IX). The soft diborane also adds to the phosphorus atom in *N*-diphenylphosphinotriphenylphosphazenes[165]:

$$(C_6H_5)_3P{=}N{-}P(C_6H_5)_2 + (BH_3)_2 \rightarrow (C_6H_5)_3P{=}N{-}\underset{\displaystyle C_6H_5}{\overset{\displaystyle C_6H_5}{\underset{|}{\overset{|}{P}}}}{:}BH_3 + BH_3 .$$

The coordination interaction of $AlX_3$ (X = H, Cl, or Br) with phosphorus(III) cyanides (X) probably involves the phosphorus atom[166].

Dialkyl-(*o*-dialkylphosphinophenyl)amines (XI) are interesting ambident systems[167]:



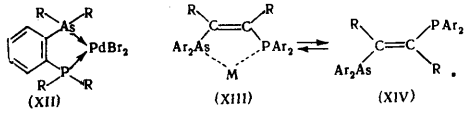
(X) (XI)

where R = alkyl or aryl. However, the formation of complexes by ligands of this type has not so far been investigated.

Here we may mention the exceptionally high electron-donating activity shown by tervalent phosphorus in ambident systems containing phosphorus and nitrogen atoms when interacting with halogens[165,168] oxygen, sulphur, selenium, tellurium[165], and other substances[165,170,171].

Quinquevalent phosphorus has almost no electron-donating properties and its derivatives are fairly active electron-acceptors[169,172]. Thus $PF_5$ is a stronger Lewis acid than $BF_3$—one of the hardest acids[173]. In agreement with this finding, ambident systems containing quinquevalent phosphorus and nitrogen behave as monodentate ligands, which form on coordination interaction complexes with exclusively M–N bonds. The complexes of phosphazenes are similar coordination compounds[174].

Phosphorus and arsenic atoms. Dialkyl-(*o*-dialkylphosphinophenyl)arsines are ambident systems containing electron-donating phosphorus and arsenic atoms, which form cyclic structures (XII) with the soft $PdBr_2$:[175]



(XII) (XIII) (XIV)

Probably metal-containing rings of this kind should be characteristic also of the *cis*-isomers of ethylene derivatives (XIII),[176] but, when the electron-donating centres in the ambident system (XIV) are in the *trans*-positions and for the *meta*- and *para*-substituted derivatives of compound (XII), it is very likely that the reaction will take place separately at the phosphorus and arsenic atoms[177]. Preferential coordination should be even more characteristic of analogous derivatives with nitrogen and phosphorus atoms and particularly of those with nitrogen and arsenic atoms[177].

b. Conjugated Systems with Electron-donating Atoms (of Group V and VI Elements)

Nitrogen and oxygen (sulphur, selenium) atoms. The simplest ambident systems containing nitrogen and oxygen systems are NO and $NO_2$ groups.

Nitrosyl complexes involve exclusively bonds with the nitrogen atom[33,38]. This conclusion was initially based mainly on infrared spectroscopic data and was recently confirmed for a series of complexes by X-ray diffraction studies[33,178].

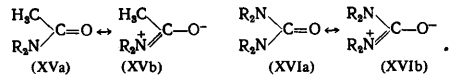
For the nitrite ion, in the study of the complexes of which salt isomerism[33,36,180] was discovered[179], two types of complexes are known: nitro-complexes in which the metal is linked to the nitrogen atom and nitrito-complexes in which a bond with the oxygen atom is formed (in the latter case cyclic structures are also possible)[33]. The majority of hard and soft metals form nitro-complexes and only a few very unusual compounds $[Ni(NO_2)_2L_X]_2$, $K_3Cu(NO_2)_5$, $K_4Ni(NO_2)_6$, etc. involve the formation of nitrito-complexes[28]. For both ions considered, the site of the coordinate bond is independent of the "hardness" or "softness" of the cations, being determined to a large extent by the ligand environment. Thus compounds of the type $ML_X(NO_2)_2$ (L = ammonia, ethylenediamine, pyridine, and its 2-amino-derivatives) are typical nitro-complexes, while 1,2-diphenylene-ethylenediamine is known to form also nitrito-complexes[33].

A similar situation arises also for cyanato-complexes[33,52]. It has been shown[52] that all the known cyanate complexes may be divided into four groups in terms of the mode of coordination of the $NCO^-$ anion: in the first group $NCO^-$ is coordinated via the nitrogen atom (isocyanates), in the second group via the oxygen atom (cyanates), the third group includes compounds with isocyanate bridges of the type $M\diagdown\!\!\diagup NCO$, and the fourth group includes compounds in which the NCO groups play the role of outer-sphere ions. The M–NCO structure has been observed for manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I), lead(II), and indium(III) in compounds of the type $M(NCO)_n mL$ (L = pyridine, 2-aminopyridine, 2,2′- or 4,4′-dipyridyl, 1,10-phenanthroline, or urotropine). The same structure is characteristic of the typical soft platinum(II) and palladium(II) cations. The NCO group interacts via the nitrogen atom also with the "soft" mercury, silver, cadmium, and copper, but in this case bridge structures are formed (the third group).

The second group of compounds, involving the M–O bond includes only a few complexes with mercury(II), molybdenum(III), rhenium(IV), and rhenium(V). Preferential coordination via the nitrogen atom, which has been frequently demonstrated by systematic infrared spectroscopic[52,69,74] and X-ray diffraction[52] studies, agrees with the high $\pi$-electronic charge at the nitrogen atom of the cyanate anion[181–183].

A different picture is observed for the amides of monocarboxylic acids (XV), which behave mainly as

monodentate ligands with the coordinate bond located at the oxygen atom[33]:

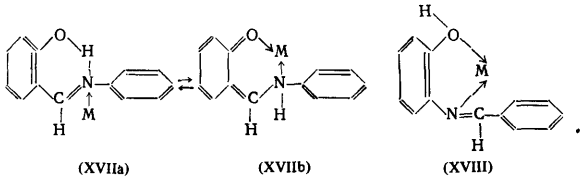


(XVa) (XVb) (XVIa) (XVIb)

Such coordination, which can be explained[184] by the enhanced electron density at the oxygen atom associated with the mesomeric effect of conjugation in (XVb), is characteristic of salts of Group I[185,186] and III–V[9,33,184,187-193] metals, the $UO_2$ cation[194-197], certain bivalent metals[198-203], and the soft platinum(II) and palladium(II)[33]. This type of coordination has been fairly convincingly demonstrated on the basis of infrared spectra (decrease of the stretching vibration frequencies of the amide bands[204]) and follows also from X-ray diffraction data[12,52] and NMR spectra[184]. The coordination interaction of $MX_n$ with aminoacetophenone[205] and *NN*-dimethylamino-derivatives of unsaturated aromatic ketones[206] takes place similarly. At the same time in a few studies it has been suggested that complexes may be formed via the nitrogen atom[207], the N–M–O bridge linkage[33], and even via the hydrogen atom attached to the carbonyl carbon atom of dimethylformamide[208,209]. The above hypotheses and particularly the last one appear to be unlikely.

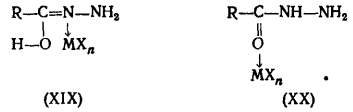
The possibility that the nitrogen and oxygen atoms of urea and its *N*-derivatives are involved in coordination interaction has been more rigorously demonstrated. It has become generally accepted[38,42,68] that, on coordination via the nitrogen atom, urea has the structure (XVIa) and the coordination via the oxygen atom is due to the mesomeric conjugation effect in (XVIb). It ought to be possible to apply successfully the HSAB principle to this compound in order to account for the location of the coordinate bond at the nitrogen atom in the complexes with the "soft" palladium and platinum[33] and at the oxygen atom in the complexes of "hard" acids[33,38,42,203,210-223]. However, the finding[224] that the "hard" $BF_3$ is coordinated at the nitrogen atom of *N*-alkyl(aryl)-substituted urea shows that in this case the HSAB concept should be employed with much caution§.

Among other ligands containing nitrogen and oxygen atoms, mention should be made of *p*-hydroxyazomethines (XVII, XVIII):



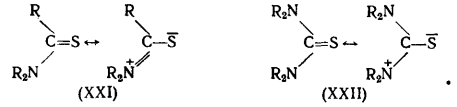
(XVIIa) (XVIIb) (XVIII)

For the complexes (XVIIa–XVIII) with $MX_X$ (M = $M^I$, $M^{II}$, $M^{III}$, $M^{IV}$, or $M^V$; X = Cl, Br, or I), the formation of the quinonoid configuration (XVIIb), where the metal is linked to the oxygen and nitrogen atoms[235,236], is quite likely to occur, as well as structures in which the metal is bound to the nitrogen atom (XVIIa, XVIII).[225-234] The data obtained in the study of the structures of the complexes of transition metal, cadmium, and zinc halides with acetyl and benzoyl hydrazides are also consistent with the above considerations[237]. However, the "imidol" structure (XIX), rather than the hydrazide structure (XX), attributed in this case to the complexes requires additional proof:



(XIX) (XX)

In contrast to nitrogen- and oxygen-containing ligands, ambident systems with nitrogen and oxygen atoms enter into coordination interactions mainly in accordance with the HSAB principle. The behaviour of the thiocyanate anion is particularly instructive in this respect. The interaction of soft metals (platinum, palladium, silver, gold, and mercury) with this anion always results in the formation of a bond via the sulphur atom[5,12,33,52,68], while hard metals are linked to the hard nucleophilic centre—the nitrogen[12,33,52,238-242]. Such preferential coordination¶ via the nitrogen or sulphur atom in the thiocyanate ion has been rigorously demonstrated by infrared spectroscopic[12,28,69,243-245] and X-ray diffraction studies[12,33,52] and has been frequently discussed as a classical example of competitive coordination[12,33]. At the same time it is regarded as proven that, regardless of their "hardness" or "softness", metals react with thioamides[33,246,247] and thiourea[248-270] to form preferentially complexes with an M–S bond. Probably, as for amides and urea, the formation of structures with strongly polarised C=S bonds (XXI–XXII) leads to a reduced electrondensity at the nitrogen atom and makes it relatively inaccessible to coordination interaction:



(XXI) (XXII)

However, it has been suggested that "soft" acids [platinum(II) and palladium(II)] are linked to the nitrogen atom in *N*-methylthiourea[271] and intermediate acids ($TiCl_4$) are linked to the nitrogen atom in thiourea itself[272]. The possible involvement of the sulphur atom in thiourea in coordination interaction with the soft $Ag^+$ cation follows also from a potentiostatic study of complexes of the type $Ag^+[(NH_2)_2CS]_n$.[273] One cannot rule out the possibility that thiourea forms with soft metals (palladium, mercury) bridge structures in which nitrogen and sulphur atoms are simultaneously involved in coordination[274,275].

The site of the coordinate bond containing nitrogen and selenium atoms is also consistent with the HSAB principles: metals of class a (hard cations) prefer the hard nitrogen atom and those of class b (soft cations) prefer the soft electron-donating centre—the selenium atom[12,33,51,52,276].

As a result of many years of systematic study by Soviet chemists[12,51,52,276], the most complete data on the competitive coordination of nitrogen and selenium atoms have been obtained for the selenocyanate ion $NCSe^-$. The results yielded by infrared spectroscopic[52,69,276] and X-ray diffraction[12,52] methods make it possible to divide[276] selenocyanate complexes into three groups: ionic selenocyanates and complexes in which the metal is linked to the nitrogen or selenium atom. Ionic selenocyanates are formed by alkali metals, strontium, barium, and thallium:

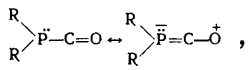
§The authors themselves[224] believe that the coordination of $BF_3$ at the nitrogen atom can be justified from the standpoint of the HSAB principle by its greater rigidity compared with the oxygen atom. However, this explanation conflicts with the coordination of the "soft" platinum(II) and palladium(II) via the nitrogen atom in urea[33].

¶One cannot exclude also the possibility of forming bridge structures in which the thiocyanate ion is linked to transition metal atoms via both electron-donating atoms[12,33].

complexes involving the selenium atom are characteristic of the soft cations of silver, gold, mercury, and the platinum metals [33,276]. The remaining metals form complexes via the nitrogen atom [12,33,276-283]. Cadmium, lead, and tervalent cobalt, which are capable of forming complexes both via the nitrogen and selenium atoms, may be regarded as an intermediate group of metals [74,276,281]. There is also a group of two-metal complexes in which the $NCSe^-$ anion behaves as a bridge [274,276]. The structure of these compounds also fits into the framework of the HSAB principle. Soft metals form a bond with selenium and hard and intermediate metals with the nitrogen atom. Thus in the complex $CoHg(SeCN)_4$ cobalt is linked to the nitrogen atom and mercury to selenium: the analogous lead derivative evidently has the same structure [276].

As was in fact to be expected, in complexes of selenourea and its *NN*-derivatives with soft metals, a linkage between the metal and selenium atom is formed [10,284,285]. This structure occurs also in mixed complexes of tervalent cobalt of the type $[Co(DM)_2Seu_2]X$ and $[Co(DM)_2(Seu)ThiO]X$, where DM = dimethylglyoxime, Seu = selenourea, ThiO = thiourea, and X = acid residue [221,286].

Phosphorus and oxygen (sulphur, selenium) atoms. As in the systems containing phosphorus and oxygen atoms, tervalent phosphorus exhibits a more pronounced electron-donating capacity than does the oxygen atom [170,171,287]. Thus the study of the infrared spectra of complexes of metal halides with the phosphides of monocarboxylic acids (XXIII) shows that, regardless of the "hardness" or "softness" of the acids, the coordinate bond involves the phosphorus atom (the stretching vibration frequencies of the C=O group increase) [287]:



(XXIII)

where R = alkyl, aryl, or arylalkyl.

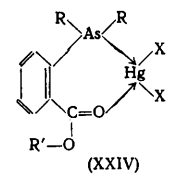
This result, which conflicts with the HSAB principle† might be explained by the conjugation of the carbonyl group with the *d* orbitals of phosphorus, which leads to the appearance of a negative charge at the phosphorus atom and a positive charge at the oxygen atom together with a decrease in the order of the C=O bond [288,289]. However, there are serious objections to such an explanation associated with the absence or an insignificant degree of $p,\pi$ conjugation in systems with tervalent phosphorus [171].

In contrast to tervalent phosphorus, quinquevalent phosphorus has almost no electron-donating properties and in systems with $\rangle P{=}X$ (X = O, S, or Se) groups, the donor–acceptor interaction involves exclusively the X atoms. There are numerous literature data concerning the coordination interactions of metals with $POCl_3$, $PSCl_3$, and $R_3P = O$ which are quoted by Webster [172] and by Bridgland and McGregor [290] and for similar interactions involving $R_3P = Se$ by Nicpon and Meck [291].

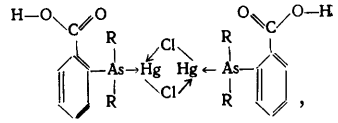
†Preferential coordination via the oxygen atom and not the phosphorus atom would be expected [1,4,16].

Arsenic and oxygen (sulphur) atoms. There are comparatively few data available for the discussion of the site of the coordinate bond in ambident systems containing tervalent arsenic and Group VI elements as electron-donating centres.

It has been shown that, in complexes of $HgX_2$ (X = Cl, Br, or I) with dialkyl(aryl)-2-carboxyphenylarsine and its derivatives, mercury is linked to the arsenic atom and the carbonyl oxygen [compound (XXIV)]: [292]



(XXIV)



(XXV)

where R = $CH_3$, $C_6H_5$, or $C_7H_7$ and R′ = H or $CH_3$ in compound (XXIV) and R = $C_6H_5$ in compound (XXV).

It has been suggested that 2-carboxyphenyldiphenylarsine forms a dimeric bridge structure in which the soft $HgCl_2$ is linked only to the soft electron-donating centre—the arsenic atom is (XXV). [292]

Like quinquevalent phosphorus, quinquevalent arsenic has no electron-donating properties and therefore in ligands of the type $R_3As = X$ (R = alkyl or aryl; X = O or S), the coordination interaction involves exclusively the X electron-donating atom [290,293-295]. This conclusion has been confirmed by studies on the complexes $R_3As{=}X \rightarrow MYn$ in the far infrared (the vibrations of the M–X bonds have been detected in the range 270 to 450 $cm^{-1}$). [296,297]

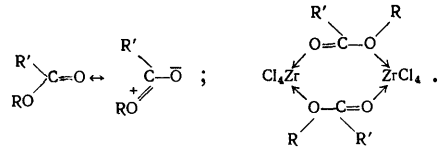
c. Ambident Systems with Identical Electron-donating Atoms

Analysis of the literature data shows that even for electron-donating atoms which are identical but subjected to different electronic and steric influences in the molecule, one may formulate the problem of competitive coordination. For such nucleophilic centres, the concepts of "hardness" and "softness" can probably retain their significance in the sense of a greater or smaller accessibility to coordination attack by electrophilic agents.

The postulate of an increased electron-donating capacity by nucleophilic atoms with increasing *p* character of the hybrid orbitals [298-300], which follows from Paulings' theory, would appear to predict an increase of preferential coordination in the following sequence of electron-donating atoms with different types of hybridisation: $sp < sp^2 < sp^3$. However, this postulate is probably valid only for isolated or non-conjugated systems. On the other hand, in ambident compounds the direction of coordination attack depends significantly on the distribution of electron density (the $\pi$-electronic densities at the nucleophilic centres), the degree of localisation of electrons at the electron-donating atoms, and steric factors.

Oxygen atoms. Numerous studies designed to establish the site of the coordinate bond in complexes of organic acids and esters with Lewis acids have shown that the oxygen of the carbonyl group is the electron-donating atom [9,16,38,42,68]. Regardless of the "hardness" or "softness" of the acids and the bulk and the electronic effect of the substituents (R and R′), the infrared spectra of the complexes (XXVI) always show a decrease of the stretching vibration frequency of the carbonyl group [301-309], which is

fairly convincing evidence [33,37] in favour of the reaction involving the carbonyl oxygen‡:

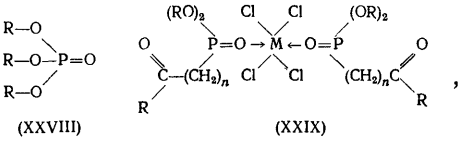


(XXVI)
R = alkyl or aryl;
R' = H, alkyl or aryl

(XXVII)
R=$C_2H_5$; R'=$CH_3$

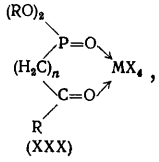
This direction of coordination attack (which contradicts Pauling's theory [311] can probably be accounted for by σ, π conjugation in compounds (XXVI), which leads to an increase in electron density at the carbonyl oxygen in esters compared with aldehydes or ketones and to a decreased capacity of the alkoxy-oxygen (the alcoholic oxygen) for participation in coordination interaction (compared with alcohols and ethers).

At the same time there is reason to suppose that not only carbonyl but also alkoxy-oxygen (alcoholic oxygen) of esters and organic acids may be involved in coordination interaction. In this case the non-planar dimers (XXVII) are formed in solution [312]. Evidently one cannot rule out the possibility of the formation in the condensed phase of coordination polymers involving the alkoxy- and carbonyl oxygen. Therefore, the conclusions concerning the site of the coordinate bond based solely on infrared spectroscopic data must be treated with caution. Dipole moments may prove very useful in solving this problem [313].



(XXVIII) (XXIX)

where M = Sn or Ti;



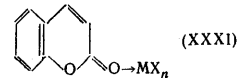
(XXX)

where M = Ti or Sn and X = Cl, Br, or I.

In alkyl phosphate complexes the coordinate bond is located solely at the oxygen of the phosphoryl group [compound (XXVIII)], [314-317] the electron-donating activity of which surpasses even that of the carbonyl group, since in complexes of α-ketophosphinic acids [318] and β-phosphonocarbonyl compounds [319] with the composition $MX_4.2L$ the coordination involves only the phosphoryl oxygen [compound (XXIX)]. On the other hand, in complexes with the composition $MX_4.L$, cyclic structures (XXX) are formed, the coordination interaction in which involves the carbonyl and phosphoryl but not the alkoxy-oxygen atoms, in agreement with the foregoing considerations [318,319].

‡In this connection one can hardly agree with the view of Pilipenko and Savranskii [301] that the carbonyl oxygen has a lower coordination capacity compared with the hydroxyl oxygen in the conjugated systems which they considered.

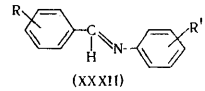
The formation of the complexes by the halides of Group III–V elements with the keto-derivatives (XXXI) involves the carbonyl oxygen [320]:



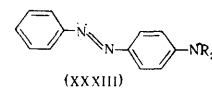
(XXXI)

where M = Ti, Sn, Zr, In, Ga, or Nb, X = Cl, Br, or I, and $n$ = 3–5.

Nitrogen atoms. The azomethines (XXXII) and the azo-compounds (XXXIII) containing an amino- or a dimethylamino-group in the aromatic ring are suitable examples for discussing the problem of the site of the coordinate bond in ambident systems with $sp^3$- and $sp^2$-hybridised nitrogen atoms:



(XXXII)
a. R = p-$N(CH_3)_2$; R' = H
b. R = m-$N(CH_3)_2$; R' = H
c. R = H; R' = m-$N(CH_3)_2$
d. R = H; R' = p-$N(CH_3)_2$
e. R = R' = p-$N(CH_3)_2$

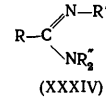


(XXXIII)
a. R = H
b. R = $CH_3$

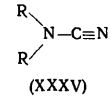
It was established on the basis of infrared and ultraviolet spectra and quantum-chemical calculations that the formation of complexes by compound (XXXII) with the chlorides of Group IV and V elements involves the nitrogen atom of the azomethine group, which has the maximum π-electron density [80].

Only in compound (XXXIIc) is the electron-donating centre the amino-nitrogen [80], which forms also quaternary salts [75]. In view of the small difference between the ultraviolet spectra of the adducts of $CuCl_2$, $CoCl_2$, and $HgCl_2$ with 4-aminoazobenzene (XXXIII, R = H) and the spectrum of the initial azo-compound, one must assume that the coordinate bond in such compounds is located at the amino-nitrogen [67,76,77]. At the same time, $BF_3$, $SnCl_4$, and $SbCl_5$ form bonds preferentially with the nitrogen atom of the azo-group [77-79].

It has recently been shown that in the amidines (XXXIV) with $sp^2$- and $sp^3$-hybridised nitrogen atoms the coordinate bonds formed on interaction with $SnCl_4$ [321] and $B(n\text{-}C_3H_7)_3$ [322] is located at the nitrogen atom of the azomethine group:



(XXXIV)



(XXXV)

where R = H, alkyl, or aryl and R' = R'' = aryl for compounds (XXXIV) and R = H or alkyl for compounds (XXXV).

Cyanamide and its *NN*-dialkylderivatives (XXXV) are the simplest ambident systems with $sp^3$- and $sp$-hybridised nitrogen atoms. On interaction with $MX_4$ (M = Sn, Ti, or Zn and X = Cl or Br), cyanamide itself behaves as a bidentate ligand, while its dialkyl derivatives are coordinated via the harder nitrogen atom of the nitrile group [323]. Probably in the case of $sp^3$- and $sp$-hybridised nitrogen atoms the direction of coordination attack is determined mainly by the negative π-electron densities§, although one

§The $sp$-hybridised nitrile nitrogen has a much higher negative π-electron charge density (−0.279) than that of the amino-nitrogen (−0.064). [324]

canot rule out the possibility that the bulky ethyl substituents prevent the location of the bond at the amino-nitrogen[325].

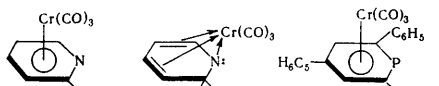
Thus the principal factor determining the mode of addition of electrophilic agents (acids) in ambident systems with several competing but identical electron-donating atoms is the magnitude of the negative $\pi$-electron charge density. This conclusion is directly related to the HSAB principal and the familiar postulate that the most nucleophilic centre in the molecule is the electron-donating atom with the highest negative potential.

d. Specific Ambident Systems

Heteroaromatic compounds. In five-membered heterocycles with a single heteroatom (furan, thiophen, selenophen, and pyrrole), which have two potential electron-donating centres (the heteroatom and the $\pi$-electron system), coordination interaction involves mainly¶ $\pi$ electrons[9,327-334].

There is at present no doubt about the validity of this conclusion: (1) metal carbonyl $\pi$ complexes of pyrrole[331,334], thiophen[335,336], and selenophen[336] have been synthesised; (2) azoferrocene has been obtained on the basis of the $\pi$-electron system of pyrrole[332,333]; (3) measurements of the dipole moments and studies on the infrared spectra of thiophen and furan complexes of $SnCl_4$ indicate the occurrence of $\pi$-electron coordination interaction[9,327-329].

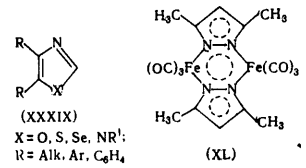
In contrast to five-membered heterocycles, six-membered heterocyclic nitrogen-containing systems (pyridine, quinoline, and many of their derivatives) react with metal salts exclusively via the nitrogen atom[337,338]. The reported synthesis of a chromium tricarbonyl $\pi$ complex of pyridine (XXXVI)[339] was disproved by the same investigators[340]†, who showed that the $\pi$ complex[339] is in fact a $\pi,\sigma$ derivative of the hydrogenated pyridine ring[340] and the amino-olefinic system (XXXVII) is involved in coordination interaction. It is interesting to note that a similar $\pi,\sigma$ bond has been attributed to the magnanese tricarbonyl derivative of pyrrole[342]. At the same time 2,4,6-triphenylphosphorine (phosphabenzene—L) forms both $\sigma$ complexes with the compositions $L(CO)_5$ and $L(CO)_4$ and the $\pi$ complex $L(CO)_3$ with the structure (XXXVIII):[343]




(XXXVI) (XXXVII) (XXXVIII)

The azoles (XXXIX)[334,345]—five-membered heterocycles with two heteroatoms one of which is nitrogen—and their aromatic analogues behave in coordination interaction like the six-membered heteroaromatic systems (pyridine) and not like the thiophen (furan, pyrrole) systems.

Azole-containing systems form mainly $\sigma$ complexes via the nitrogen atom of the azole ring with Group II,[346-349] III,[350-353] IV,[354-359] and V[357-358] metal salts, Group III metal derivatives[359,360], and Group VI metal carbonyls[361-363]



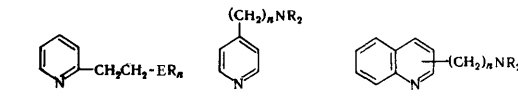

(XXXIX) X = O, S, Se, $NR^1$; R = Alk, Ar, $C_6H_4$ (XL)

However, objections have been made against the involvement in the coordination interaction of the $\pi$-electron system of the azole ring[364] and the electron pair of the X heteroatom[365] and therefore we believe that additional tests are required. The properties of the 3,5-dimethylpyrazole complex of iron carbonyl can be accounted for not only from the standpoint of $\pi$ complex formation but also by the formation of the dimeric structure (XL), resembling that of the complexes of pyrazole with $BF_3$[366] and $AlR_3$.[359,360]

The hypothesis concerning the possible coordination via the X heteroatoms conflicts with the familiar postulate that $sp^3$-hybridised O, S, Se atoms and NR groups of azoles have no electron-donating properties[344,367]. Moreover, the negative $\pi$-electronic charge density is almost wholly localised at the nitrogen atom (the X atom is positively charged), which, was shown above to constitute the principal factor responsible for the location of the coordinate bond at the competing heteroatoms of the ambident system‡.

Thus, according to published data, heteroaromatic systems behave predominantly as monodentate ligands: five-membered systems (pyrrole, thiophen, furan, and selenophen) are $\pi$-electron donors and six-membered nitrogen containing systems and azoles are $\sigma$-electron donors.

Derivatives of heteroaromatic systems. The non-conjugated systems (XLI–XLIV) form several classes of complexes[368-374]:




(XLI-XLII) (XLI): E = P, As, N: R = Alk. Ar; $n = 2$ (XLII): E = O, S: R = H, Alk; $n = 1$ (XLIII) R = H, Alk, Ar. $n = 1, 2$ (XLIV) R = H, Alk: $n = 1, 2$

Nickel(II), cobalt(II), and zinc(II) salts form cyclic structures with 2-($\beta$-diphenylphosphinoethyl)pyridine (XLI, E = P) involving the nitrogen and phosphorus atoms[368]. On the other hand, when there is a considerable difference in hardness, for example between the nitrogen and arsenic atoms, the above salts interact only with the nitrogen atom, while the soft copper(I) halides interact with the "soft" arsenic atom[369].

¶There is some evidence for the possibility of the quaternisation of the sulphur atom of thiophen[326]. The hydrogenated five-membered systems readily form $\sigma$-complexes via the heteroatom[9,327-330].

†Unfortunately this erroneous study was employed by Candlin et al. in their monograph[341] as an example of a $\pi$ complex of a heterocyclic ring.

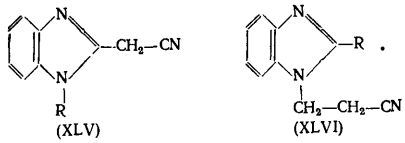
‡The high negative $\pi$-electron charge density at the oxygen atom of oxazole[367] suggests that the coordination interaction with "hard" cations ($BF_3$, $AlX_3$) may take place via this atom.

In a study of complex formation in a series of 2-[$\beta$-hydroxy(mercapto)ethyl]pyridines (XLII), it was noted[370] that the coordinate bond with relatively soft $MX_2$ is located at the nitrogen of the pyridine ring and not at the harder oxygen and sulphur atoms.

It is believed that $\alpha$-substituted aminoethylpyridines (XLI, E = N) can form complexes of three types: (1) cyclic compounds with transition metals involving both electron-donating centres[371-374]; (2) complexes with $NiI_2$ involving only the amino-nitrogen[371]; (3) complexes of Group IV metal (tin and titanium; $n$ = 2) tetrachlorides[375] and niobium oxide trichloride[376] involving the nitrogen atom of the pyridine ring.

$\gamma$-Derivatives of pyridine (quinoline) also form complexes of $MX_4$ and $NbOCl_3$ via the nitrogen atom of the pyridine (quinoline) ring[357,375,376]. These results in general agree with the greater hardness of $MX_4$ and $NbOCl_3$ compared with $NiI_2$ (in addition to the greater softness of the metal itself[13], the symbiotic effect[4,14] of the soft iodide anion probably operates in this case). However, it is noteworthy that Uhlig and Maeser[371] did not study the infrared spectroscopic behaviour of the pyridine ring and therefore their results should be treated with some caution.

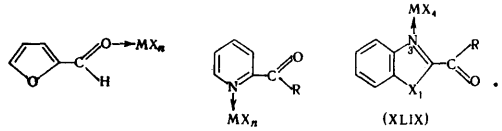
In complexes of $SnCl_4$ and $TiCl_4$ with cyano-derivatives of the benzazole series (XLV, XLVI), coordination interaction probably involves the softer nitrogen atom of the azole ring[377]:



(XLV) (XLVI)

$MX_n$ forms complexes via the oxygen atom with carbonyl derivatives of five-membered heteroaromatic system having one heteroatom. Stable neutral complexes of furfural with $MX_4$ have been isolated[378,379], their infrared spectra showing a considerable decrease in the frequency of the carbonyl stretching vibrations indicating that the coordinate bond involves the carbonyl oxygen [compound (XLVII)].[37,68]

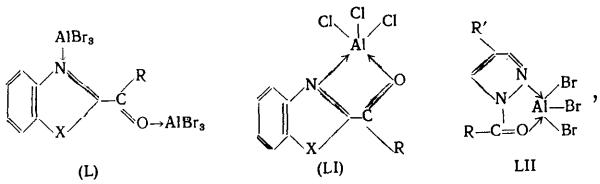
On the other hand, the formation of complexes via the nitrogen atom is characteristic of pyridyl ketones (XLVIII)[380] and carbonylazoles (XLIX)[353,377,381] containing electron-donating nitrogen and oxygen atoms:



(XLVII) (XLVIII) (XLIX)

R = H, Alk, Ar. $X_1$ = S, NR

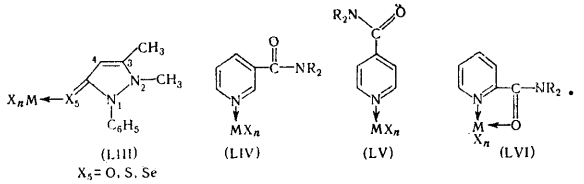
Only with $AlX_3$ (X = Cl or Br) and carbonylazoles can coordination interaction involve both electron-donating centres with the formation of complexes (L) having the composition $2AlBr_3$.(L) or, under favourable steric conditions, of cyclic compounds of types (LI) and (LII)[83,353,356,381]



(L) (LI) LII

where X = S or $NCH_3$ and R = H or $CH_3$.

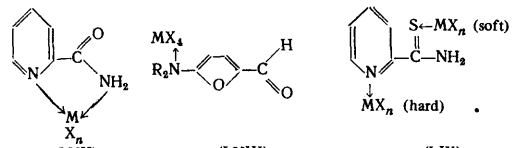
Antipyrine (LIII) and its derivatives should seemingly be included among nitrogen- and oxygen-containing ambident systems. However, the localisation of a high negative $\pi$-electron charge at the oxygen atom[81,382-384] renders antipyrine a monodentate ligand in which coordination interaction involves exclusively the exocyclic oxygen atom regardless of the type of $MX_n$.[81,384-391] Thio- and seleno-antipyrines behave similarly[81,389]:



(LIII) (LIV) (LV) (LVI)

$X_5$ = O, S, Se

The coordination interactions of $MX_n$ with pyridine-carboxylic acid amides and thioamides is unusual. Nicotinamide (LIV) and isonicotinamide (LV) form complexes with the coordinate bond involving preferentially the nitrogen atom of the heterocyclic ring[380,392,393]. On the other hand, depending on the composition of the complexes and the properties of $MX_n$, picolinamide forms cyclic structures in which complex formation involves the pyridine nitrogen and the carbonyl oxygen [compound (LVI)][394] or the amino-nitrogen [compound (LVII)][395-397].



(LVII) (LVIII) (LIX)

The coordinate bond in the complexes of the tetrachlorides of Group IV elements with 5-(*N*-dialkylamino)-furfurals (LVIII) involves mainly the amino-nitrogen and not the carbonyl oxygen[399]. Whereas the direction of coordination attack in ambident systems containing nitrogen and oxygen atoms is difficult to predict§, in pyridine-carboxylic acid thioamides soft acids (Au, Ru, Os, Ag, and Rh) attack the "soft" sulphur atom and the harder transition metal salts attack the nitrogen atom [compound (LIX)], in agreement with the HSAB principle[400].

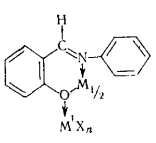
In the series of amino-,[82,348,353,401,402] azomethine[80,82], azo-,[348,403-405] and cyano-derivatives[406-407] of pyridine and azoles, the coordinate bond is preferentially¶ located at the electron-donating centre with the highest negative $\pi$-electronic charge[80,82], as for the aliphatic and aromatic ambident systems with nitrogen atoms hybridised in different ways.

Metal chelate ambident systems. It has been shown[409-411] that metal chelates may be used as ligands in complex formation ("complexes as ligands",[411-412] "complexes of complexes"[413,414]). The problem of the location of the coordinate bond in such dinulcear complexes arose at once[409-419]. It is believed[409,411-415,417] that coordination interaction involves the oxygen atoms of

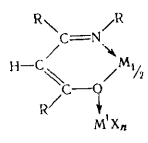
§In pyridine-2-acetamide, which has non-conjugated electron-donating centres, the coordinate bond is located in accordance with the HSAB principle: $PdX_2$ (X = Cl or Br) enters into coordination interaction with the soft nitrogen atom, while the harder $MX_2$ interact with the nitrogen and oxygen atoms[398].

¶It is believed that the formation of complexes with 2-amino-1,3,4-oxadiazole involves the amino-group[408].

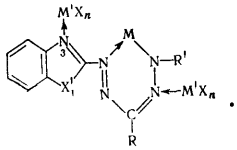
the metal chelate unit of the inner-complex compounds of the Schiff bases (LX) and β-aminovinyl ketones (LXI). However, the investigators[410,416,418,419] concluded that the interaction of $SnCl_4$ and $TiCl_4$ with salicylideneanilinato-complexes leads to the rupture of the metal-containing ring and the location of the bond at the nitrogen atom of the azomethine group:



(LX): M = Ni, Cu; M' = Ni, Cu, Ti, Sn



(LXI): M = Ni, Co; M' = Sn, Ti



(LXII): M = Ni, Cu; M' = Sn, Ti; X = Cl, Br; $X_1$ = O, S, $NR'$

In the metal chelates of the formazans of the benzazole series, the centres for the formation of a donor–acceptor bond with $MCl_4$ (M = Sn or Ti) are probably not only the nitrogen atom of the heterocyclic ring but also the nitrogen atoms of the formazan ring [compound (LXII)].[420]

The problem of competitive intramolecular coordination in metal chelates (the building up of square-planar and tetrahedral structures to octahedral structures) is probably directly related to these data. However, its discussion is outside the scope of the present review.

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The HSAB principle is a simple and convenient formulation of a number of postulates relating to acid–base interaction and not a new law or theory. The main postulates of the HSAB principle are extremely useful for a systematic arrangement and explanation of experimental data accumulated on the problem of the location of the coordinate bond in systems with several electron-donating centres. A general description of data on competitive coordination in non-conjugated systems from the standpoint of the HSAB principle is particularly desirable (unfortunately fewest studies have been made precisely in this field).

For conjugated (ambident) systems, the concepts of the "hardness" and "softness" of the electron-donating atoms are extremely arbitrary: the nitrogen and oxygen atoms, which have been assigned by Pearson to the same class of hard bases, can function as soft nucleophilic centres, while the "soft" sulphur can become hard (thiourea, thioamides, thioantipyrine). Similarly in many cases the terminological concepts of "hardness" and "softness" lose their significance in the case of cations. Probably, in a consideration of the problem of competitive coordination in ambident systems, one cannot in general relate the concepts of the "hardness" and "softness" of nucleophilic atoms to the Schwarzenbach, Chatt, and Pearson classifications. In estimating the "softness" and "hardness" of electron-donating centres, it is more correct to take into account the properties characterising the "soft" and "hard" nucleophilic agents as defined by Pearson†. In the same connection, one should evidently assume that in any polyfunctional system it is possible to isolate centres for the preferential formation of a donor–acceptor bond. As shown above, the position of such a centre coincides in general with that of the electron-donating atom bearing the highest negative π-electron charge density.

†Regardless of its position in the Periodic System, any atom can evidently exhibit Pearson's "hard" or "soft" properties.

The experimental data discussed in the present review indicate the unusually pronounced interest in the problem of competitive coordination among both Soviet and foreign investigators. At the same time there have been still too few systematic and comprehensive discussions of the causes of a particular mode of coordination in polyfunctional ligands‡. In many cases the experimental data are insufficient for this purpose (a narrow selection of "acids" and "bases"), while in others (these include the majority of investigations) the aim of the study was to discover the location of the bond at a particular electron-donating atom.

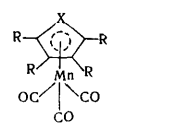
The tasks of the immediate future are probably specific synthesis of polydentate ligands with electron-donating centres of different types and specific selection of acids (both "hard" and "soft") for the solution and a comprehensive examination of the problem of competitive coordination. Such attempt designed to synthesise ligands are already being made[177,421] and they must be prosecuted in all possible ways. Naturally, the successful solution of the problem depends on the reliability of the experimental methods employed for this purpose.

A general description of data on competitive coordination in the chemistry of complex compounds may prove extremely useful in determinations of the mode of reactions in polyfunctional systems and for other branches of chemistry. We believe that the study of the problem of the location of the hydrogen bond and of the site of protonation of organic compounds with several electron-donating centres is particularly promising; the data which have accumulated[422–437] show that, in agreement with the HSAB principle, this process involves the hardest atom in non-conjugated and ambident systems. The question of the quaternisation of polyfunctional systems, primarily the amino-, azomethine, and azo-derivatives of nitrogen-containing heterocycles, is apparently closely related to this problem.

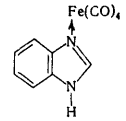
## ADDENDUM

(to Section III, subsection 3d)

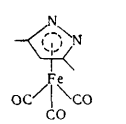
π-Complexes of manganese tricarbonyl with tetraphenylphosphole (LXIII) and tetraphenylarsenole (LXIV) have been synthesised[438]:



(LXIII): X = P; R = $C_6H_5$
(LXIV): R = $C_6H_5$; X = As



(LXV)



(LXVI): R = H, $CH_3$

Complexes (LXV) in which the ligand behaves as a monodentate base and is coordinated to the metal via the "pyridine" nitrogen atom have been described. Complexes (XL)[439,440] and (LXVI)[430] have been synthesised and the structure of a π-complex has been suggested for the latter[439].

Direct proof of the location of the coordinate bond at the "pyridine" nitrogen atom in benzazoles has been obtained in a study of $^{14}N$ NMR spectra of metal carbonyl complexes of azoles[441].

‡We believe that this problem has been most satisfactorily solved for pseudohalide ions[12,258,276].

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