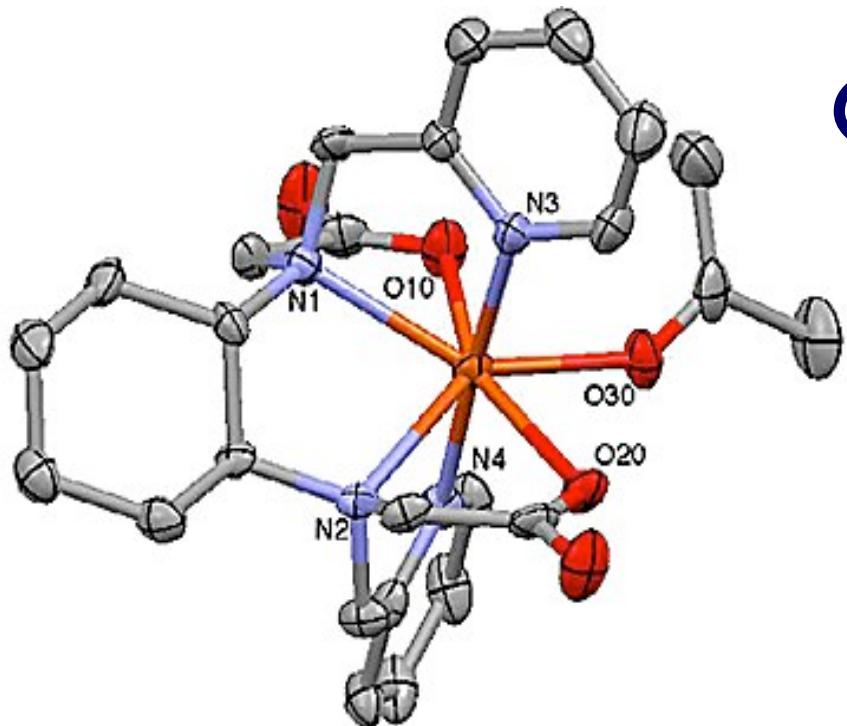


QUÍMICA INORGÂNICA 1

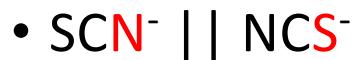
2020-2021



Afinidade Química
Teoria de Pearson (HS|AB):
ácidos e bases de Lewis

Carlos Lodeiro
Dep. de Química FCT UNL

Porque, como e por onde coordena?



$\text{Cu(II)}/\text{Cu(I)}$; $\text{Hg(I)}/\text{Hg(II)}$; $\text{Co(II)}/\text{Co(III)}$

Que complexos formam?



Sal



Complexo



Afinidade Metal-Ligando

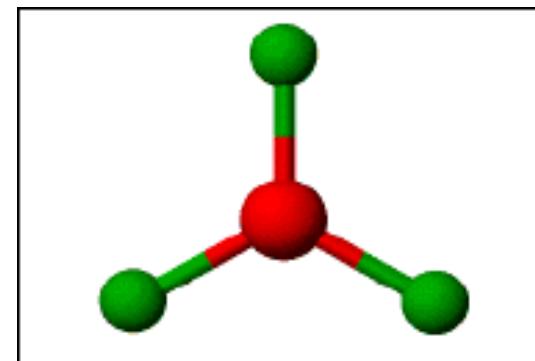
- Ácidos e Bases de Lewis
 - Teoria dos Ácidos e Bases Duros e Macios (*Hard and Soft Acids and Bases – HSAB*)
 - Teoría de PEARSON
-
- Metal \Rightarrow Ácido
 - Ligando \Rightarrow Base

Ca^{2+} Mg^{2+} Cu^{2+} Fe^{2+} Fe^{3+} Co^{2+} Ni^{2+} Mn^{2+} Cr^{3+} Ag^+ Zn^{2+} Pb^{2+} Al^{3+}

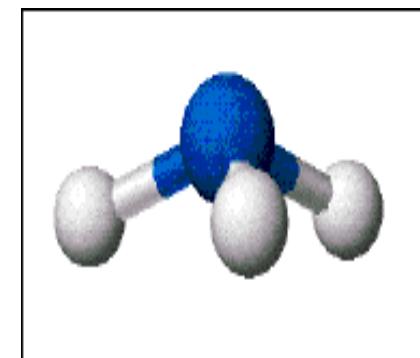


Ácidos e Bases de Lewis

- Ácido de Lewis = aceitador de um par de electrões (BF_3)



- Base de Lewis = doador de um par de electrões (NH_3)



Ácidos e Bases de Lewis

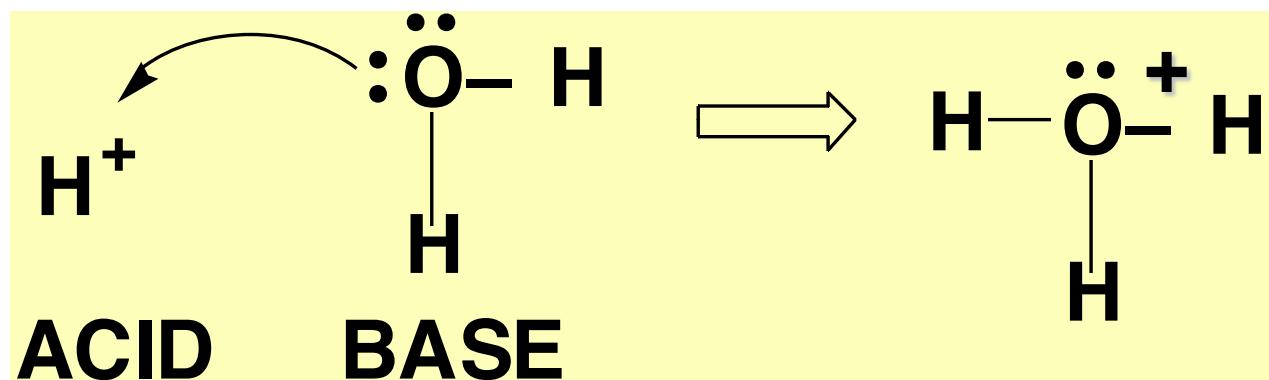
Um ácido de Lewis interage com uma base de Lewis por partilha de um par de electrões.



Ácidos e Bases de Lewis

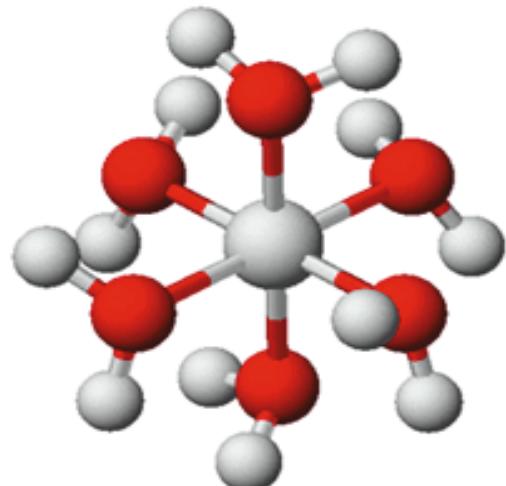
Um par ácido-base de Lewis interage por partilha de um par de electrões.

A formação do **ião hidrónio** é um excelente exemplo.



Ácidos e Bases de Lewis

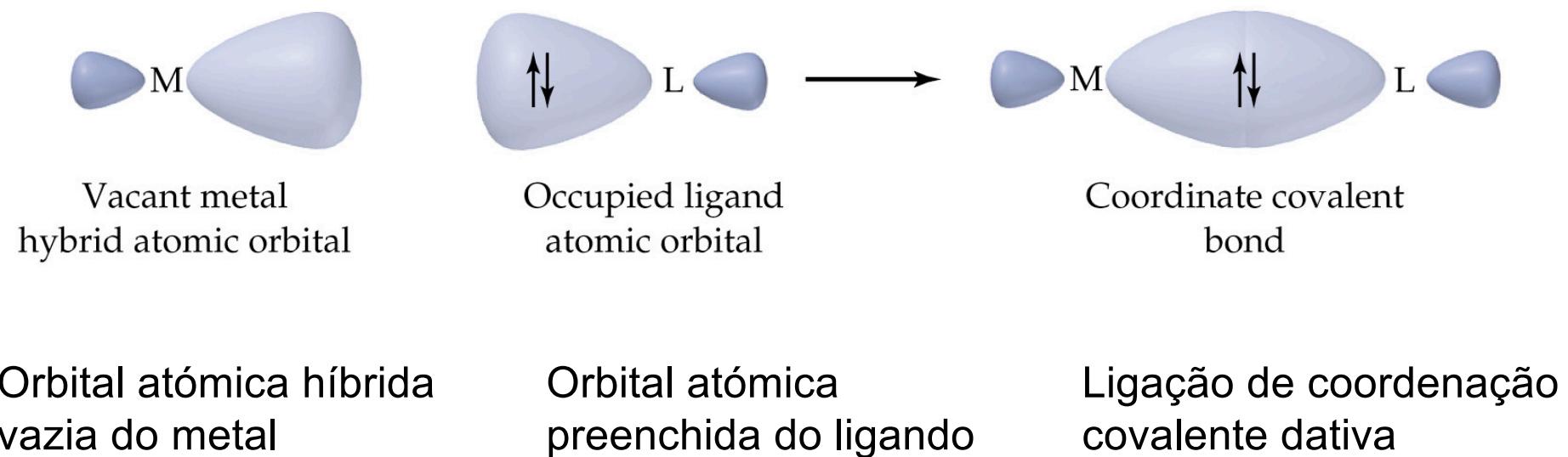
A formação de um composto de coordenação também é uma reacção ácido-base de Lewis.



Metal = Ácido

Ligando = Base

Ácidos e Bases de Lewis



Ácidos de Lewis

- Uma espécie que contenha um átomo com carga positiva com uma orbital de valência total ou parcialmente desocupada, pode funcionar como ácido de Lewis, sendo aceitadora de um par de electrões.
- Catiões: H^+ ; $(\text{CH}_3)_3\text{C}^+$; Fe^{3+} ; Cu^{2+} ; Ni^{2+} ; Hg^{2+} ; Ag^+
- Espécies neutras:
 - CO_2 ; SnCl_2 ; SO_3 , o átomo central liga-se a átomos terminais eletronegativos e fica com uma carga parcial positiva.
 - BF_3 ; AlCl_3 ; PF_5 , o átomo central tem carga parcialmente positiva e tem pelo menos uma orbital de valência desocupada

Bases de Lewis

- São espécies que contêm átomos com pares de electrões disponíveis. Tais átomos denominam-se **átomos doadores**, sendo doadores desse par de eletrões. = Ligandos.

- **Monodentadas:**

- Aniões: OH^- ; O^{2-} ; S^{2-} ; H^- ; X^- ;
- Neutras: H_2O ; NH_3 ; CO ; olefinas

- **Espécies polidentadas:**

- Apresentam mais que um átomo doador (etilenodiamina; EDTA), dien; tren; phen; bpy; etc.



Identifique os ácidos e bases de Lewis nas seguintes reações:

- $\text{BrF}_3 + \text{F}^- \Rightarrow [\text{BrF}_4]^-$
 - O ácido BrF_3 adiciona a base $:\text{F}^-$
- $\text{KH} + \text{H}_2\text{O} \Rightarrow \text{KOH} + \text{H}_2$
 - KH fornece a base (ião hidreto = H^-) para deslocar o ácido H^+ da molécula de água
- $[\text{:SnCl}_3]^- + [\text{Mn}(\text{CO})_5]\text{Cl} \Rightarrow (\text{CO})_5\text{Mn-SnCl}_3 + \text{Cl}^-$
 - Ácido/Base $[\text{Mn}(\text{CO})_5]^+ / [\text{:SnCl}_3]^-$

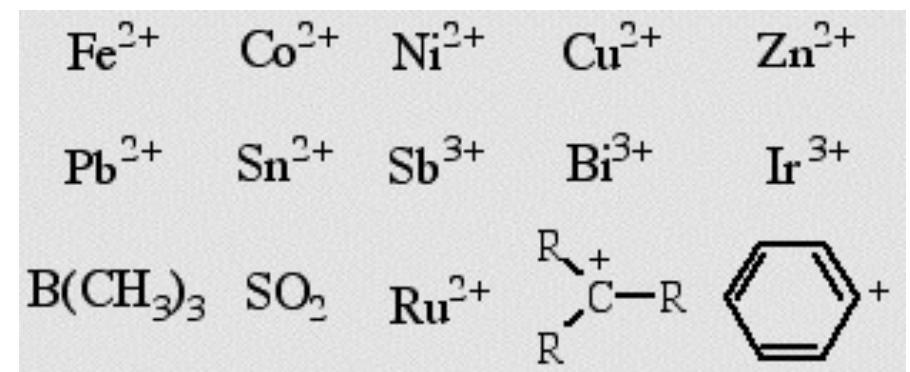
Ácidos e Bases Duros e Macios (HSAB) teoria de pearson

Método de classificação de catiões metálicos e ligandos em compostos de coordenação que permite prever quais os ligandos que têm mais afinidade por determinado metal:

- **DUROS**: Nuvem electrónica da espécie não se forma, **fraca polarizabilidade**
- **MACIOS**: Nuvem electrónica facilmente deformável, **elevada polarizabilidade**

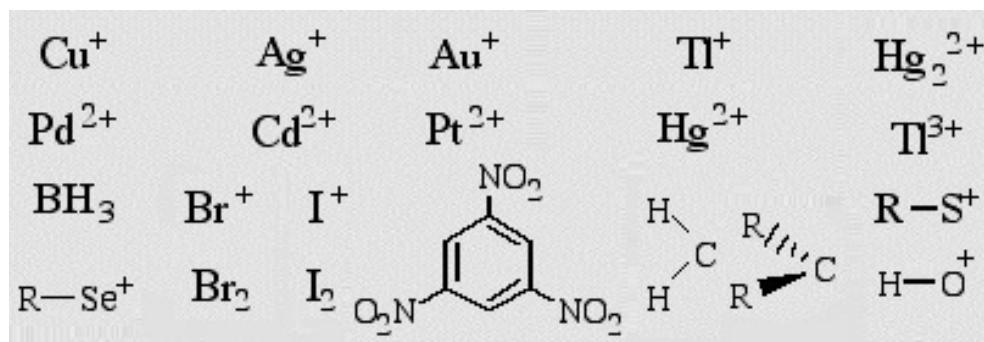
Ácidos de Lewis

H^+	Na^+	K^+	Be^{2+}	Mg^{2+}
Ca^{2+}	Mo^{3+}	Mn^{2+}	Al^{3+}	Sc^{3+}
In^{3+}	Cr^{3+}	Co^{3+}	Fe^{3+}	Ti^{4+}
Zr^{4+}	U^{4+}	Ce^{3+}	Sn^{4+}	BF_3
AlCl_3	AlH_3	SO_3	NO_2^+	CO_2



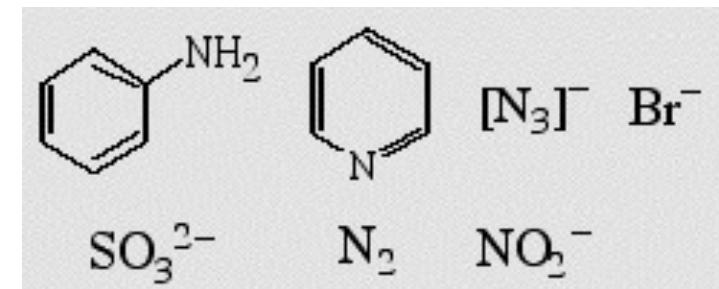
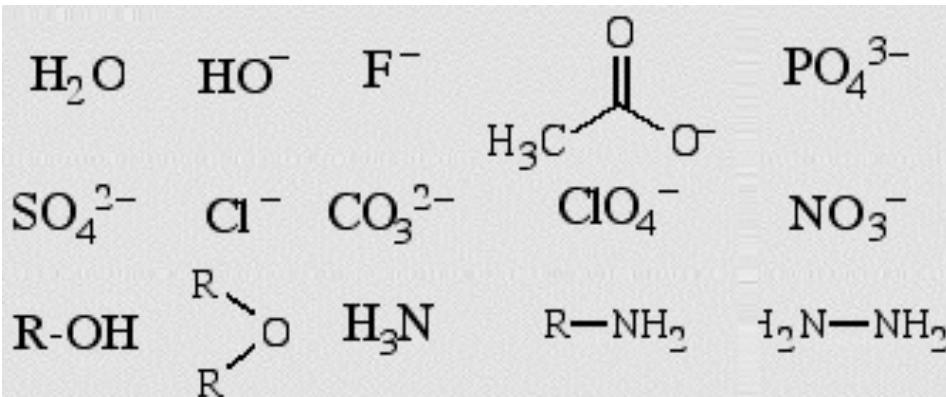
Duros

Intermédios



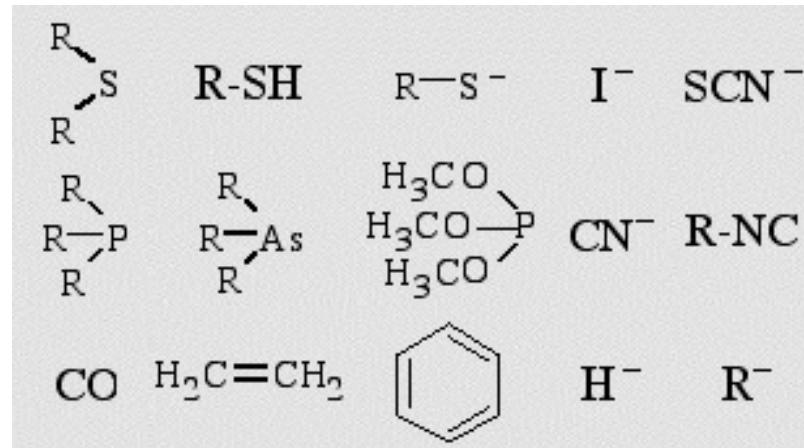
Macios

Bases de Lewis



Duras

Intermédias



Macias

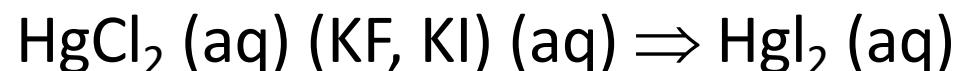
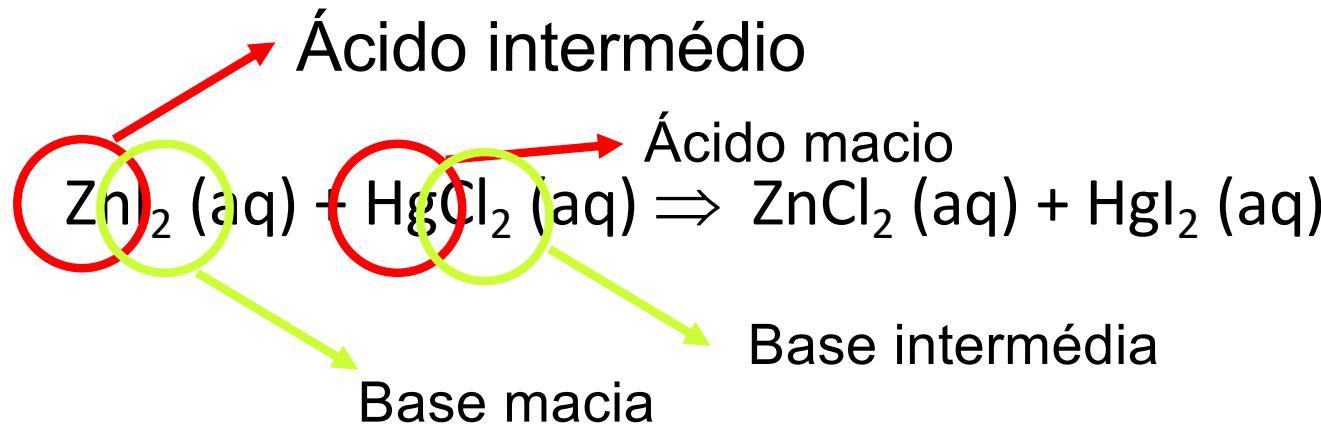
Ácidos e Bases **Duros** e Macios (HSAB)

“Os ÁCIDOS DUROS coordenam preferencialmente BASES DURAS, e os ÁCIDOS MACIOS coordenam preferencialmente BASES MACIAS”

DUROS com DURAS
MACIOS com MACIAS



Quais os produtos das seguintes reacções?



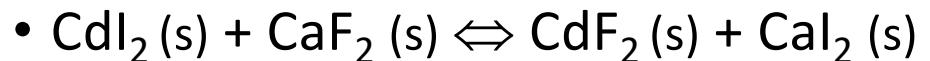


Quais os complexos que se formarão numa solução aquosa contendo Hg^{2+} , Cl^- , Na^+ e I^- ?

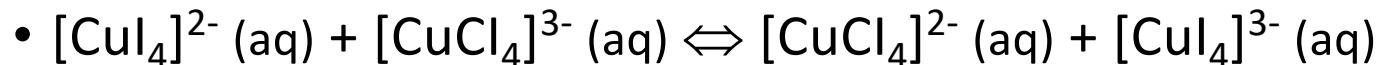
Ácidos	Bases	Complexos
Hg^{2+} (ácido macio)	I^- (base macia)	HgI_2
Na^+ (ácido duro)	H_2O (base dura)	$[\text{Na}(\text{H}_2\text{O})_6]^+$
H_2O (ácido duro)	Cl^- (base intermédia)	$(\text{H}_2\text{O})_n \text{Cl}^-$



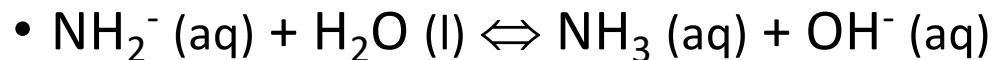
Preveja se as constantes de equilíbrio das seguintes reacções serão maiores ou menores que 1.



$K_{\text{eq}} < 1$; deslocado no sentido dos reagentes



$K_{\text{eq}} > 1$; deslocado no sentido dos produtos



$K_{\text{eq}} > 1$; deslocado no sentido dos produtos



Quais os complexos que se formarão numa solução aquosa contendo NO_3^- , Ag^+ , Cl^- e K^+ ?

Ácidos	Bases	Complexos ou sais
Ag^+ (ácido macio)	Cl^- (base intermédia)	AgCl
K^+ (ácido duro)	H_2O (base dura)	$[\text{K}(\text{H}_2\text{O})_6]^+$
H_2O (ácido duro)	NO_3^- (base dura)	$(\text{H}_2\text{O})_n \text{NO}_3^-$

INFLUENCIA NAS CONSTANTES DE ESTABILIDADE

Table 1. Formation constants with halide ions for a representative hard, soft, and intermediate metal ion .

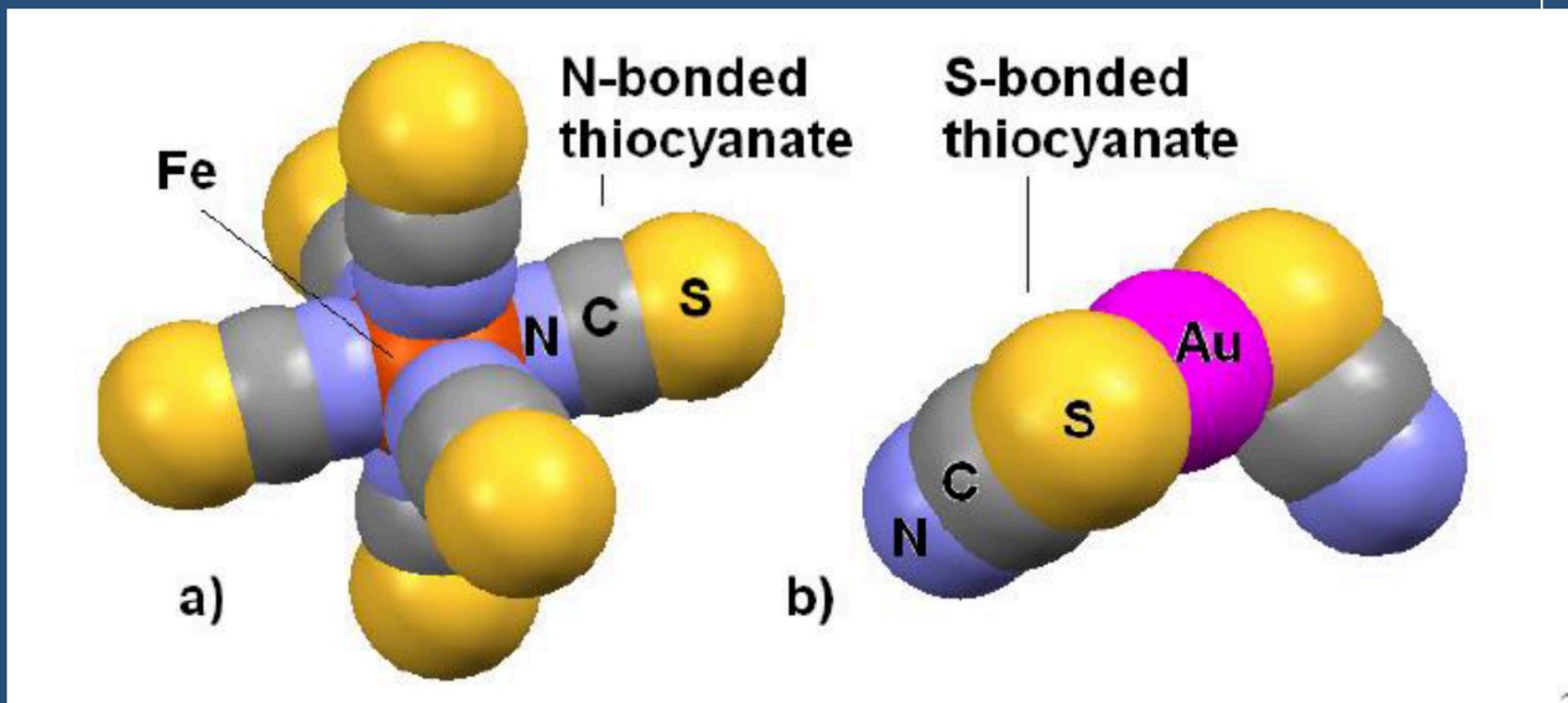
Log K_1	F^-	Cl^-	Br^-	I^-	classification
Ag^+	0.4	3.3	4.7	6.6	soft
Pb^{2+}	1.3	0.9	1.1	1.3	intermediate
Fe^{3+}	6.0	1.4	0.5	-	hard

INFLUENCIA NAS CONSTANTES DE ESTABILIDADE

Metal ion:	Ag^+	Ga^{3+}	Pb^{2+}
Log $K_1(\text{OH}^-)$:	2.0	11.3	6.0
Log $K_1(\text{SH}^-)$:	11.0	8.0	6.0

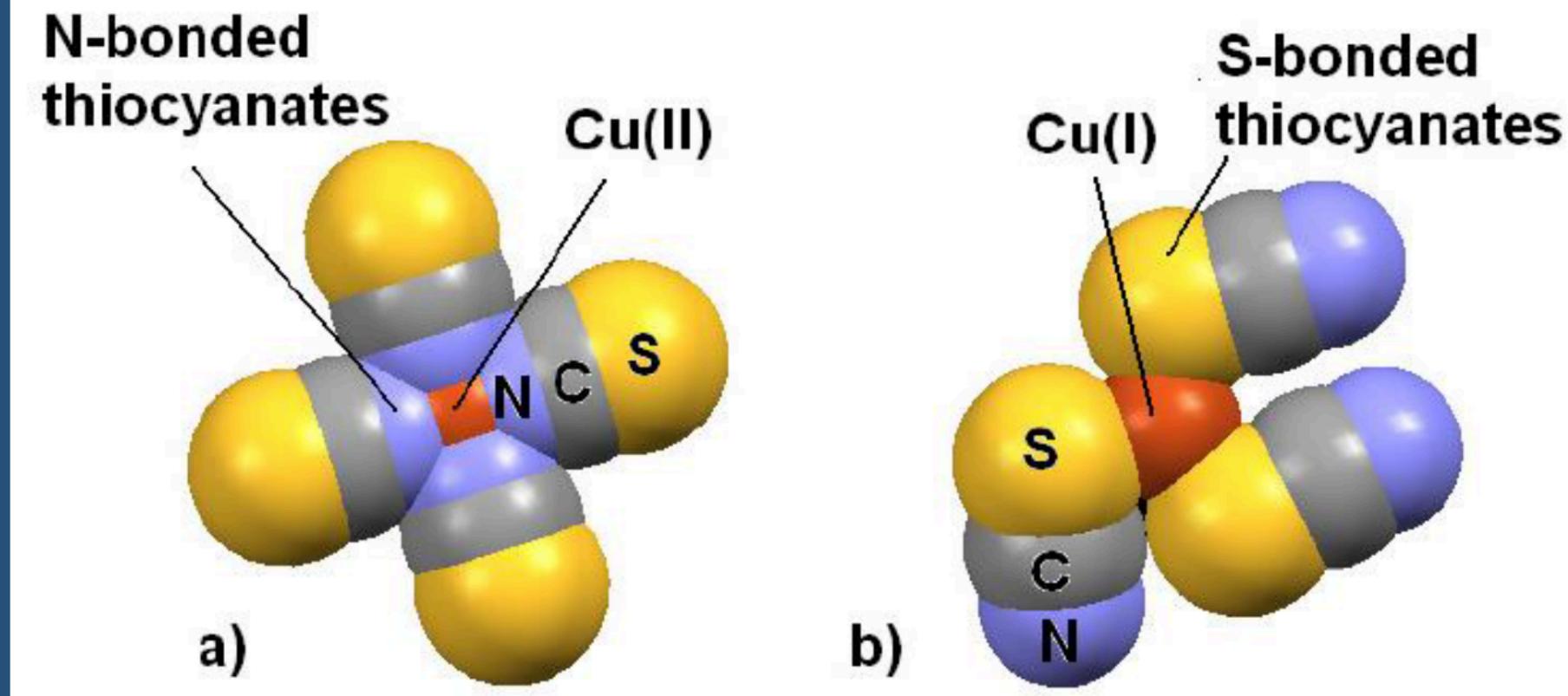
- O ácido Ag^+ é macio e prefere a base SH^- , também macia, relativamente à base dura OH^- .
- O ácido duro Ga^{3+} prefere a base dura OH^- relativamente à base macia SH^- .
- O ácido intermédio Pb^{2+} não tem preferência definida.

Ligando tiocianato ou isotiocianato?



- Ligação através do N no complexo com Fe^{3+} (isotiocianato) - $[\text{Fe}(\text{NCS})_6]^{3-}$
- Ligação através do S no complexo com Au^{3+} (tiocianato) - $[\text{Au}(\text{SCN})_2]^-$.

Cu(II) ou Cu(I)



- Ligação através do N no complexo com Cu^{2+} , um ácido intermédio $[\text{Cu}(\text{NCS})_4]^{2-}$
- Ligação através do S no complexo com Cu^+ , um ácido macio $[\text{Cu}(\text{SCN})_3]^{2-}$.

Tabela de Aminoácidos

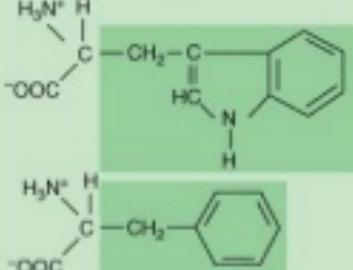
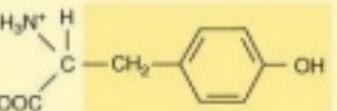
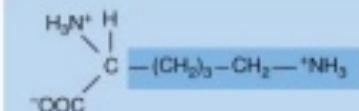
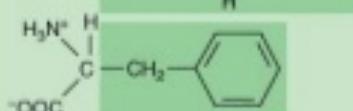
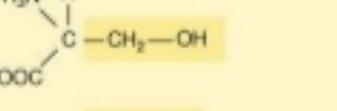
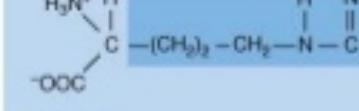
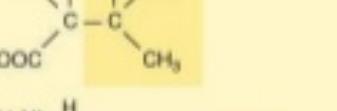
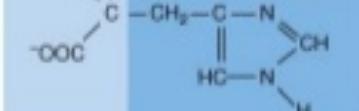
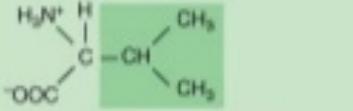
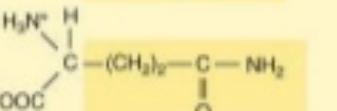
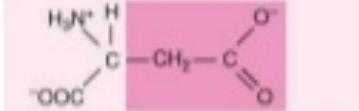
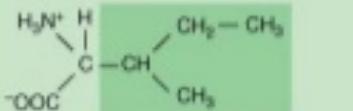
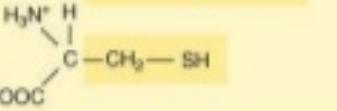
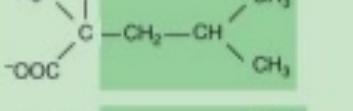
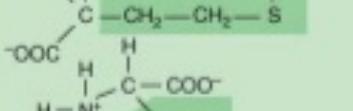
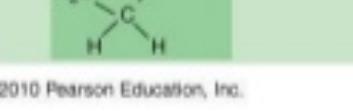
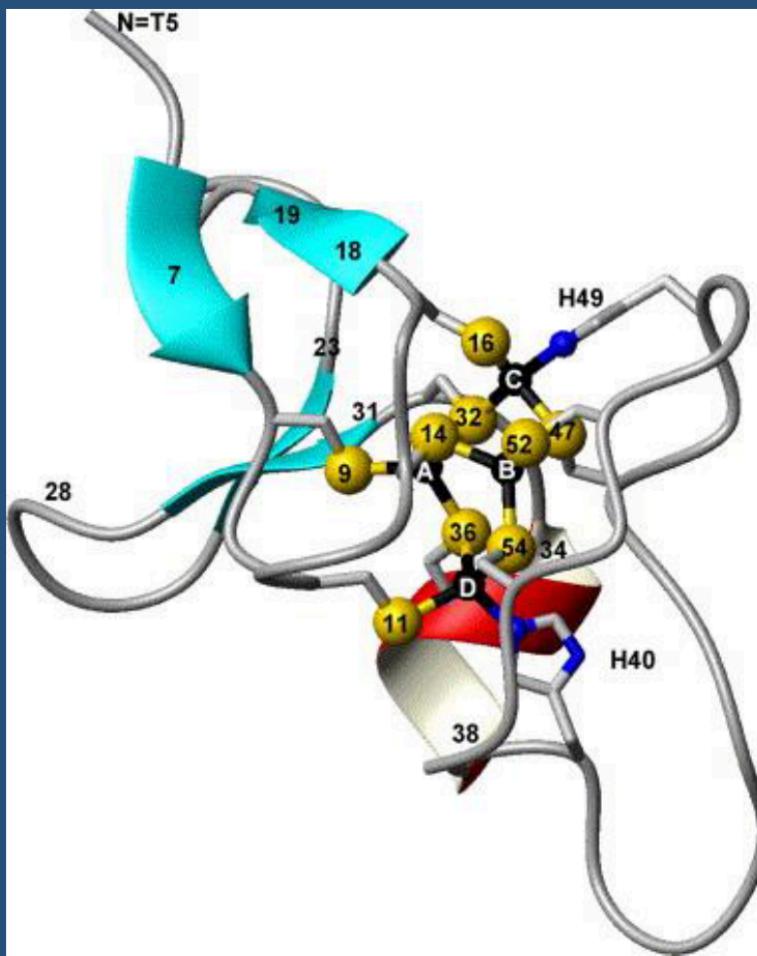
Neutral, nonpolar	Neutral, polar	Basic	Acidic
 <p>Tryptophan (Trp) (W)</p>	 <p>Tyrosine (Tyr) (Y)</p>	 <p>Lysine (Lys) (K)</p>	
 <p>Phenylalanine (Phe) (F)</p>	 <p>Serine (Ser) (S)</p>	 <p>Arginine (Arg) (R)</p>	
 <p>Glycine (Gly) (G)</p>	 <p>Alanine (Ala) (A)</p>	 <p>Threonine (Thr) (T)</p>	
 <p>Valine (Val) (V)</p>	 <p>Asparagine (Asn) (N)</p>	 <p>Histidine (His) (H)</p>	
 <p>Isoleucine (Ile) (I)</p>	 <p>Glutamine (Gln) (Q)</p>		
 <p>Leucine (Leu) (L)</p>	 <p>Cysteine (Cys) (C)</p>		
 <p>Methionine (Met) (M)</p>			
 <p>Proline (Pro) (P)</p>			

Tabela de aminoácidos.
Classificados por natureza química e polaridade.

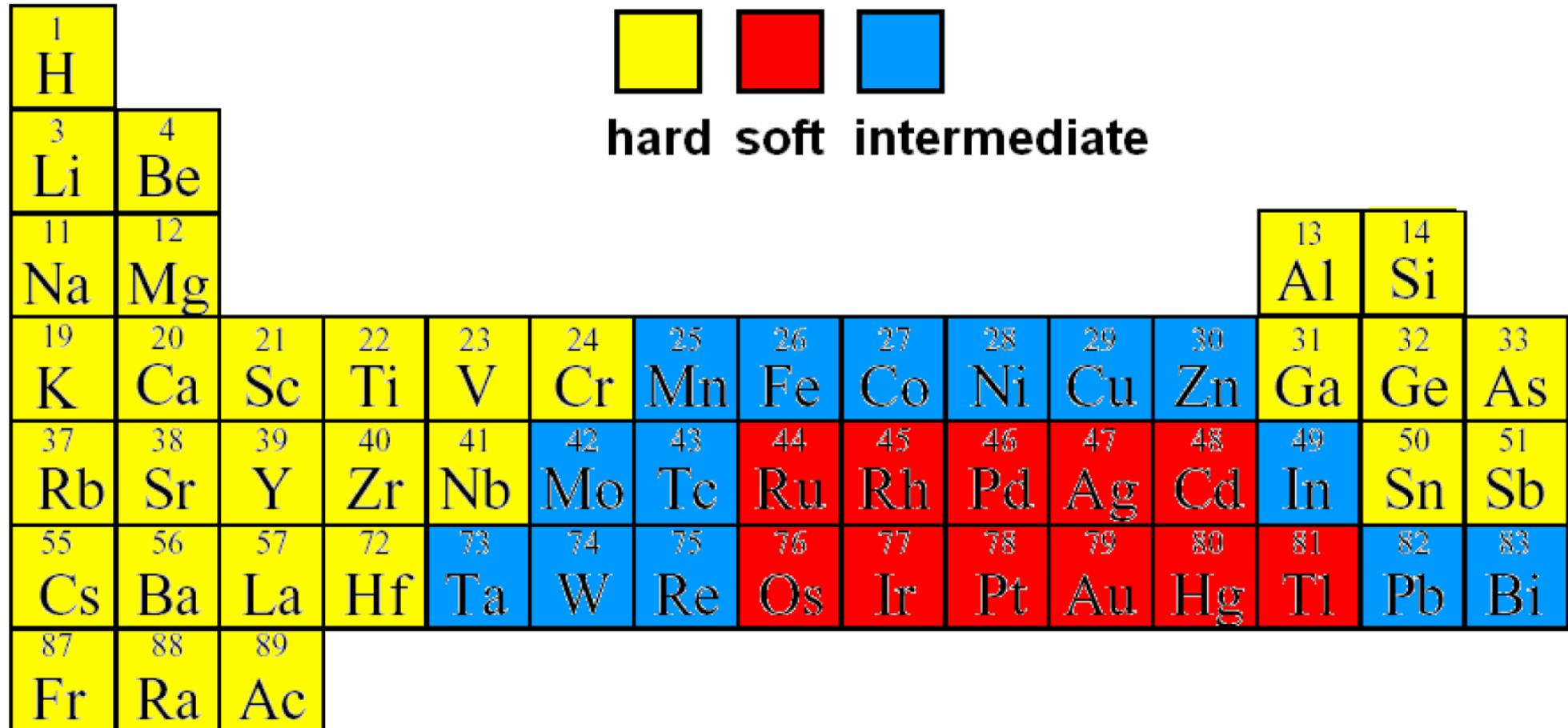
METALOTIONEINAS

Metalotioneínas – Proteínas desintoxicantes de Zn(II), Cd(II), Hg(II), Pb(II)



Leszczyszyna, O. I., et al , Inorganica Chimica Acta, 360(1), 3–13

Distribuição na Tabela Periódica de Ácidos de Lewis duros, macios e intermédios (contribuição de Pearson)



Composto	Ligandos	Átomos doadores dos ligandos	Contração	Número de coordenação do metal	Configuração eletrônica	Geometria de coordenação do metal	Natureza do Átomo central	Natureza dos Ligandos
$\text{Na}[\text{MnCl}_4]$	Cloro	Cloreto	Na^+	4	$3d^4$	Tetraédrica	Mn(III) Duro	Duro
$[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$	NH_3 , amin	N	Cl^-	6	$3d^2$	Octaédrica	Cr(III) Duro	Duro
$[\text{Ni}(\text{en})_3]\text{SO}_4$	Em, dietilen..	N	SO_4^{2-}	6	$3d^8$	Octaédrica	Ni(II) Intermedio	Dura
$[\text{NiBr}_2(\text{PEt}_3)_2]$	Br, PEt_3 Trietilfosfina	Br, P	-	4	$3d^8$	(trans) Plana Quadrangular (cis)Tetraédrica	Ni(II) Intermedio	Br Intermedio P Mole
$\text{K}[\text{Au}(\text{CN})_2]$	CN	C	K^+	2	$5d^{10}$	Linear	Au(I) Mole	C Mole N intermedio
$[\text{Cu}(\text{NH}_3)_4(\text{SH}_2)_2]\text{I}_2$	SH_2 , NH_3	S, e N	I^-	6	$3d^9$	Octaédrica	Cu(II) Intermedia	N Intermedio S Mole
$[\text{Hg}(\text{SH}_2(\text{CH}_2)_2\text{NH}_2)_3]\text{F}_2$	$\text{SH}_2(\text{CH}_2)\text{NH}_2$	S, N	F^-	6	$5d^{10}$	Octaédrica	Hg(II) Macio	S Mole N Intermedio
$[\text{Ca}(18\text{-crown-6})]\text{F}_2$	18-crown-6	O	F	6	S^2	Octaédrica	Ca(II) Duro	O, Duro
$[\text{PtCl}_2(\text{SePr}_3)_2]$	Cl, SePr_3 Tripropilseliana	Cl, Se	Neutro	4	$5d^8$	(trans) Quadrangular Plano / (cis) Tetraédrica	Pt(II) Mole	Se, Mole Cl Intermedio
$[\text{Fe}(\text{phen})_3](\text{ClO}_4)_3$	Fenantrolina	N	ClO_4^-	6	$3d^5$	Octaédrica	Fe(III) duro	N Intermedio
$[\text{Co}(\text{OH}_2)_5\text{Br}]\text{Br}_2$	Br, NH_3	Br, O	Br-	6	$3d^6$	Octaédrica	Co(III) duro	O / duro Br / Intermedia

Reactividade & Afinidade

- A teoria de Pearson como vimos agrupa os metais e os ligandos em ácidos e bases de Lewis duros e macios.
- Escreva todos os complexos possíveis que dará lugar as reações seguintes tendo em conta a TP. Identifique a natureza dura ou macia do ião metálico e dos potenciais ligandos, e proponha as estruturas
- Ag(I), SH₂, H₂O, NO₃⁻, CN⁻
- Au(I), CN⁻, SH₂(CH₂)₂NH₂, H₂O, BF₄⁻
- Cu(II), acac, NO₂⁻, Cl⁻
- Ca(II), H₂O, EDTA⁴⁻, ClO₄⁻
- Fe(III), CO₂, Phen, en, F⁻
- Hg(II), tu, F⁻, SCN⁻
- Pt(II), PPh₃, Br⁻, NH₂(CH₂)₃NH₂



JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

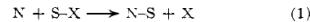
Hard and Soft Acids and Bases

BY RALPH G. PEARSON

RECEIVED JUNE 14, 1963

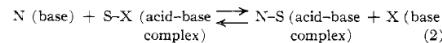
A number of Lewis acids of diverse types are classified as (a) or (b) following the criterion of Ahrlund, Chatt, and Davies. Other auxiliary criteria are proposed. Class (a) acids prefer to bind to "hard" or nonpolarizable bases. Class (b) acids prefer to bind to "soft" or polarizable bases. Since class (a) acids are themselves "hard" and since class (b) acids are "soft" a simple, useful rule is proposed: hard acids bind strongly to hard bases and soft acids bind strongly to soft bases. The explanations for such behavior include: (1) various degrees of ionic and covalent σ -binding; (2) π -bonding; (3) electron correlation phenomena; (4) solvation effects.

In a recent publication¹ the rate data for the generalized nucleophilic displacement reaction were reviewed and analyzed.



Here N is a nucleophilic reagent (ligand, Lewis base) and S-X is a substrate containing a replaceable group X (also a base) and an electrophilic atom (Lewis acid) S. Other groups may also be bound to S. It was found that rates for certain substrates, S-X, were influenced chiefly by the basicity (toward the proton) of N, and other substrates had rates which depended chiefly on the polarizability (reducing power, degree of unsaturation) of N.

In this paper the equilibrium constants of eq. 1 will be considered, instead of the rates.



Thus the relative strengths of a series of bases, N, will be compared for various acids, S. The reference base X will be constant for each comparison. In solution X may simply be the solvent, and in the gas phase X may be completely absent. Thus the discussion of equilibrium constants is concerned only with the stability of acid-base adduct N-S and the stability of the free (or solvated) base N. The nature of N-S may be that of a stable organic or inorganic molecule, a complex ion, or a charge transfer complex. In all cases it will be assumed that N is acting in part as an electron donor and S as an electron acceptor so that a coordinate, covalent bond between N and S is formed. Other types of interaction, sometimes stronger, sometimes weaker, may occur. These will be discussed later.

In terms of equilibria, rather than rates, it again turns out that various substrate acids fall into two categories: those that bind strongly to bases which bind strongly to the proton, that is, basic in the usual sense; those that bind strongly to highly polarizable or unsaturated bases, which often have negligible proton basicity. Division into these two categories is not absolute and intermediate cases occur, but the classification is reasonably sharp and appears to be quite useful. It will be convenient to divide bases into

two categories, those that are polarizable, or "soft," and those that are nonpolarizable, or "hard."² Now it is possible for a base to be both soft and strongly binding toward the proton, for example, sulfide ion. Still it will be true that hardness is associated with good proton binding. For example, for the bases in which the coordinating atom is from groups V, VI, and VII (the great majority of all bases), the atoms F, O, and N are the hardest in each group and also most basic to the proton. The reason for this has been discussed in reference 1. The atoms in each group become progressively softer with increasing atomic weight. They bind protons less effectively, but increase their ability to coordinate with certain other Lewis acids.

For the special case of metal ions as acids, Ahrlund, Chatt, and Davies³ made a very important and useful classification. All metal ions were divided into two classes depending on whether they formed their most stable complexes with the first ligand atom of each group, class (a), or whether they formed their most stable complexes with the second or a subsequent member of each group, class (b).⁴ Thus the following sequences of complex ion stability are very often found

- (a) N > P > As > Sb > Bi
- (b) N << P > As > Sb > Bi
- (a) O > S > Se > Te
- (b) O << S ~ Se ~ Te
- (a) F >> Cl > Br > I
- (b) F < Cl < Br << I

The classification is very consistent in that a metal ion of class (b) by its behavior to the halides, for example, will also be class (b) with respect to groups V and VI also.

Note that nothing is said concerning relative stabilities of group V ligands vs. group VI, for example, for a given metal ion. For a typical class (b) metal ion the order of decreasing stability of complexes for different ligand atoms is generally found to be C ~ S >

(2) The descriptive adjectives "hard" and "soft" were suggested by Professor D. H. Busch of Ohio State University.

(3) S. Ahrlund, J. Chatt, and N. R. Davies, *Quart. Rev. (London)*, **12**, 265 (1958).

(4) The terms (a) and (b) appear to have no significance except that most class (b) metal ions belong to B subgroups of the periodic table.

TABLE I
CLASSIFICATION OF LEWIS ACIDS

Class (a) or hard

H⁺, Li⁺, Na⁺, K⁺
Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Sn²⁺
Al³⁺, Sc³⁺, Ga³⁺, In³⁺, La³⁺
Cr³⁺, Co³⁺, Fe³⁺, As³⁺, Ir³⁺
Si⁴⁺, Ti⁴⁺, Zr⁴⁺, Th⁴⁺, Pu⁴⁺,
VO²⁺
UO₂²⁺, (CH₃)₂Sn²⁺
BeMe₂, BF₃, BCl₃, B(OR)₃
Al(CH₃)₃, Ga(CH₃)₃, In-(CH₃)₃
RPO₂⁺, ROPO₂⁺
RSO₂⁺, ROSO₂⁺, SO₃
I⁷⁺, I⁵⁺, Cl⁷⁺
R₃C⁺, RCO⁺, CO₂, NC⁺
HX (hydrogen bonding molecules)

Borderline

Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺,
Zn²⁺, Pb²⁺
B(CH₃)₃, SO₂, NO⁺

Class (b) or soft

Cu⁺, Ag⁺, Au⁺, Tl⁺, Hg⁺, Cs⁺
Pd²⁺, Cd²⁺, Pt²⁺, Hg²⁺, CH₃Hg⁺
Tl³⁺, Tl(CH₃)₃, BH₃
RS⁺, RSe⁺, RTe⁺
I⁺, Br⁺, HO⁺, RO⁺
I₂, Br₂, ICN, etc.
Trinitrobenzene, etc.
Chloranil, quinones, etc.
Tetracyanoethylene, etc.
O, Cl, Br, I, R₃C(?)
M⁰ (metal atoms)
Bulk metals

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