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Application of the Hard and Soft Acids and Bases Concept to Explain Ligand Coordination in Double Salt Structures

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The coordination polyhedra in 43 double salt structures are examined. Each structure is formed by at least two kinds of polyhedra. The differences in the environment around the metal ions are explained using HSAB concept. The values of hardness for 25 cations are calculated according to Klopman. A factor $\chi = H_{\text{acid}} \cdot H_{\text{base}}$, where H is the hardness value, is introduced. The value of this factor can be used as a criterion for the stability of the complexes. The possibilities which the χ factor gives in explaining ligand coordination in known structures as well as for predicting structures for double salts are illustrated.

Introduction

In a previous paper (*1*) the HSAB (Hard and Soft Acids and Bases) concept (*2*) was successfully applied to explain ligand coordination in the structures of hydrates of some bivalent metal halides. It was shown that H_2O molecules and halide ions compete for coordination states around the metal ions and that hard cations such as Mg^{2+} and Ca^{2+} show a pronounced affinity for coordination with the harder ligands while soft cations such as Cd^{2+} prefer coordination with softer ligands.

It is interesting to apply this idea to the double salt hydrates where there is a competition between two ligands for positions in the coordination polyhedra of both metal ions. We have examined 43 structures of double salts of the type $Me_mMe'_nL_x \cdot yH_2O$, where the valence of Me and Me' can be from +2 to +4 and L is F or Cl. The coordination polyhedra which form the structures of these salts are shown in Table I.

Experimental

As in our previous paper (*1*) we will use "softness" (and "hardness," resp.) of acids and bases as defined by Klopman (*3*). In Table II are listed the values of hardness for 25 cations calculated using the procedure of Klopman. Klopman's values (*3*) for ligand hardness are listed in Table III.

The data in Table I show that in absolutely all cases the harder cation coordinates with the harder ligands and the softer cation with softer ligands. For example, in $ZnSiF_6 \cdot 6H_2O$ the hard Si^{4+} coordinates with six F^- (the harder ligand) while the softer Zn^{2+} is surrounded by six softer H_2O molecules. In the same way, in $CdMg_2Cl_6 \cdot 12H_2O$ the hard Mg^{2+} coordinates only with H_2O molecules (the harder ligand) and the soft Cd^{2+} coordinates only with Cl^-, the softer ligand. In some of the structures the environment around one or both cations is mixed. Nevertheless, the same tendency is observed in these cases. For example, in

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TABLE I

Coordination Polyhedra in Double Salt Structures

Formula	Polyhedra	Reference
$CdGaF_5 \cdot 7H_2O$	$[Cd(H_2O)_6][GaF_5(H_2O)]$	*(14, 15)*
$ZnInF_5 \cdot 7H_2O$	$[Zn(H_2O)_6]_2[In(H_2O)_2F_4][InF_6]$	*(15)*
$Cd_2ZrF_8 \cdot 6H_2O$	$[CdF_4(H_2O)_3]_2[ZrF_8]$	*(16)*
$Mn_2ZrF_8 \cdot 6H_2O$	$[MnF_4(H_2O)_3]_2[ZrF_8]$	*(17)*
$MnZrF_6 \cdot 5H_2O$	$[MnF_2(H_2O)_4][ZrF_8]$	*(18)*
$CuTiF_6 \cdot 4H_2O$	$[CuF_2(H_2O)_4][TiF_6]$	*(19)*
$CuZrF_6 \cdot 4H_2O$	$[CuF_2(H_2O)_4][ZrF_6]$	*(19)*
$CuSiF_6 \cdot 4H_2O$	$[CuF_2(H_2O)_4][SiF_6]$	*(19, 20)*
$NH_4CuTiF_7 \cdot 4H_2O$	$[CuF_2(H_2O)_4][TiF_6]$	*(21)*
$NH_4CuSiF_7 \cdot 4H_2O$	$[CuF_2(H_2O)_4][SiF_6]$	*(21)*
$ZnZrF_6 \cdot 6H_2O$	$[Zn(H_2O)_6][ZrF_6]$	*(22)*
$ZnSiF_6 \cdot 6H_2O$	$[Zn(H_2O)_6][SiF_6]$	*(22, 23)*
$CoSiF_6 \cdot 6H_2O$	$[Co(H_2O)_6][SiF_6]$	*(24)*
$FeSiF_6 \cdot 6H_2O$	$[Fe(H_2O)_6][SiF_6]$	*(25)*
$MgSiF_6 \cdot 6H_2O$	$[Mg(H_2O)_6][SiF_6]$	*(20)*
$Mg(BF_4)_2 \cdot 6H_2O$	$[Mg(H_2O)_6][BF_4]_2$	*(26)*
$Mn(BF_4)_2 \cdot 6H_2O$	$[Mn(H_2O)_6][BF_4]_2$	*(26)*
$Fe(BF_4)_2 \cdot 6H_2O$	$[Fe(H_2O)_6][BF_4]_2$	*(26)*
$Co(BF_4)_2 \cdot 6H_2O$	$[Co(H_2O)_6][BF_4]_2$	*(26)*
$Ni(BF_4)_2 \cdot 6H_2O$	$[Ni(H_2O)_6][BF_4]_2$	*(26)*
$Zn(BF_4)_2 \cdot 6H_2O$	$[Zn(H_2O)_6][BF_4]_2$	*(26)*
$Cd(BF_4)_2 \cdot 6H_2O$	$[Cd(H_2O)_6][BF_4]_2$	*(26)*
$MgGeF_6 \cdot 6H_2O$	$[Mg(H_2O)_6][GeF_6]$	*(27)*
$FeGeF_6 \cdot 6H_2O$	$[Fe(H_2O)_6][GeF_6]$	*(27)*
$CoGeF_6 \cdot 6H_2O$	$[Co(H_2O)_6][GeF_6]$	*(27)*
$NiGeF_6 \cdot 6H_2O$	$[Ni(H_2O)_6][GeF_6]$	*(27)*
$ZnGeF_6 \cdot 6H_2O$	$[Zn(H_2O)_6][GeF_6]$	*(27)*
$CdGeF_6 \cdot 6H_2O$	$[Cd(H_2O)_6][GeF_6]$	*(27)*
$NiBeF_4 \cdot 6H_2O$	$[Ni(H_2O)_6][BeF_4]$	*(28)*
$CoBeF_4 \cdot 6H_2O$	$[Co(H_2O)_6][BeF_4]$	*(28)*
$ZnBeF_4 \cdot 6H_2O$	$[Zn(H_2O)_6][BeF_4]$	*(28)*
$(NH_4)_2Co(BeF_4)_2 \cdot 6H_2O$	$[Co(H_2O)_6][BeF_4]_2$	*(29)*
$(NH_4)_2Ni(BeF_4)_2 \cdot 6H_2O$	$[Ni(H_2O)_6][BeF_4]_2$	*(29)*
$(NH_4)_2Zn(BeF_4)_2 \cdot 6H_2O$	$[Zn(H_2O)_6][BeF_4]_2$	*(29)*
$(NH_4)_2Cd(BeF_4)_2 \cdot 6H_2O$	$[Cd(H_2O)_6][BeF_4]_2$	*(29)*
$CaMg_2Cl_6 \cdot 12H_2O$	$[CaCl_6][Mg(H_2O)_6]_2$	*(30, 31)*
$CdMg_2Cl_6 \cdot 12H_2O$	$[CdCl_6][Mg(H_2O)_6]_2$	*(32)*
$CdNi_2Cl_6 \cdot 12H_2O$	$[CdCl_6][Ni(H_2O)_6]_2$	*(33)*
$Cd_2NiCl_6 \cdot 12H_2O$	$[CdCl_5(H_2O)]_2[Ni(H_2O)_6]$	*(34)*
$Cd_2MgCl_6 \cdot 12H_2O$	$[CdCl_5(H_2O)]_2[Mg(H_2O)_6]$	*(35)*
$Cd_4NiCl_{10} \cdot 10H_2O$	$[CdCl_6]_2[CdCl_5(H_2O)]_2[Ni(H_2O)_6]$	*(36)*
$Ca_2Cd_3Cl_{10} \cdot 18H_2O$	$[Ca(H_2O)_8]_2[CdCl_6]_3$	*(37)*
$Ca_2CdCl_6 \cdot 12H_2O$	$[Ca(H_2O)_7Cl]_2[CdCl_6]$	*(38)*

the $MnZrF_6 \cdot 5H_2O$ structure the harder cation, Zr^{4+}, is surrounded only by the harder ligands F^- while the softer Mn^{2+} by two F^- and four H_2O. In $ZnInF_5 \cdot 7H_2O$ the softer Zn^{2+} is surrounded only by the softer H_2O ligands while the harder In^{3+} forms two kinds of octahedra. In the first kind of octahedron In^{3+} is surrounded only by the harder F^- and in the second kind by four F^- and two H_2O. In $CdGaF_5 \cdot 7H_2O$ the soft Cd^{2+} coordinates only with the softer H_2O while the hard Ga^{3+} coordinates with five F^- and one H_2O.

We are interested in defining a quantitative factor which will predict the probable complex to be formed in any particular structure. To this end we introduce a numerical factor characteristic of each complex which will provide a criterion for judging the stability of the complex. The hardness of cations (H_{acid}) we equate with the $E_n^\ddagger$ values in Table II. The hardness of ligands (H_{base}) we define to be $H_{\text{base}} = -9 - E_m^\ddagger$ (see Table III). If H_{acid} and H_{base} are defined in this manner, one can see that hard cations and ligands possess positive values of H and soft cations and ligands negative H values. Then, the tendency of a hard cation to prefer a hard ligand and a soft cation to prefer a soft ligand can be expressed in the simplest way be the function $\chi = H_{\text{acid}} \cdot H_{\text{base}}$.

The combination hard cation–hard ligand as well as soft cation–soft ligand leads to a positive value of χ. Furthermore the harder are both cation and ligand (or the softer both may be), the more stable will be their complex and the higher the value of χ will be.

We suggest the following procedure for explanation of the ligand coordination in double salt structures. First, for a $Me_mMe'_n L_x \cdot yH_2O$ salt the coordination numbers for both cations against both ligand atoms must be determined. This is performed using Goldschmidt–Pauling's radii ratio rule. Then, the χ-factor for all possible metal–ligand combinations must be calculated as $\chi_i = H_a \cdot H_b$. Taking into account the coordination numbers determined and the chemical formula, all possible complexes must be composed. For each particular one, the χ must be calculated as a sum of the χ_i-values of all metal–ligand bonds taking part in the respective complex: $\chi = \Sigma_i \chi_i = \Sigma_i (H_a \cdot H_b)_i$. For each possible structure, i.e., combination of complexes (polyhedra), the total χ is again a sum of the χ-

TABLE II

HARDNESS VALUES FOR CATIONS

X^z	$X^z \leftrightarrow X^{z-1}$ energy (eV)	$X^{z-1} \leftrightarrow X^{z-2}$ energy (eV)	Orbital energy (eV)	Pauling's r (Å)	$r + 0.82$ (Å)	Desolvation (eV)	$E_n^\ddagger = H_{acid}$ (eV)
Si^{4+}	45.13	33.49	42.22	0.41	1.23	53.43	11.21
Zr^{4+}	34.33	22.98	31.49	0.80	1.62	40.56	9.07
B^{3+}	37.92	25.15	34.73	0.20	1.02	41.79	7.06
Ge^{4+}	44.70	34.21	42.08	0.53	1.35	48.68	6.60
Al^{3+}	28.44	18.82	26.04	0.50	1.32	32.27	6.23
Ti^{4+}	43.24	27.47	39.30	0.68	1.50	43.81	4.51
Be^{2+}	18.21	9.32	15.98	0.31	1.13	20.43	4.45
La^{3+}	19.17	11.43	17.24	1.15	1.97	21.62	4.38
Mg^{2+}	15.03	7.64	13.18	0.65	1.47	15.71	2.53
Ca^{2+}	11.87	6.11	10.43	0.99	1.81	12.76	2.33
Fe^{3+}	30.64	15.93[a]	26.96	0.64	1.46	29.19	2.23
Sr^{2+}	11.03	5.69	9.69	1.13	1.95	11.84	2.15
Ba^{2+}	10.00	5.21	8.80	1.35	2.17	10.64	1.84
Ga^{3+}	30.70	20.51	28.15	0.62	1.44	29.60	1.45
Cr^{2+}	14.73[a]	7.85[a]	13.01	0.83	1.65	13.99	0.98
Mn^{2+}	15.35[a]	8.17[a]	13.56	0.80	1.62	14.25	0.69
Fe^{2+}	15.93[a]	8.47[a]	14.07	0.75	1.57	14.71	0.64
Co^{2+}	16.49[a]	8.74[a]	14.55	0.72	1.54	14.99	0.44
In^{3+}	28.03	18.86	25.74	0.81	1.63	26.15	0.41
Ni^{2+}	17.01[a]	8.96[a]	15.00	0.69	1.51	15.29	0.29
Cu^{2+}	17.57[a]	9.05[a]	15.44	0.72	1.54	14.99	−0.55
Zn^{2+}	17.96	9.39	15.82	0.74	1.56	14.80	−1.02
Cd^{2+}	16.90	8.99	14.93	0.97	1.79	12.89	−2.04
Tl^{3+}	29.80	20.42	27.45	0.95	1.77	24.08	−3.37
Hg^{2+}	18.75	10.43	16.67	1.10	1.92	12.03	−4.64

[a] Refers to ionization of *s* orbitals. The values are calculated using (*13*).

TABLE III

LIGAND HARDNESS VALUES

Ligand	$E_m^\ddagger$ (eV)	H_{base}
F^-	−12.18	3.18
H_2O	−10.73	1.73
OH^-	−10.45	1.45
Cl^-	−9.94	0.94
Br^-	−9.22	0.22
CN^-	−8.78	−0.22
SH^-	−8.59	−0.41
I^-	−8.31	−0.69
H^-	−7.37	−1.63

values for the complexes which build the structure. The highest value of the total χ is an indication for the highest stability of the respective structure and this must be the real one.

The following examples illustrate the possibilities which the χ-factor gives in explaining ligand coordination in known structures as well as for predicting structures for double salt systems which have not yet been investigated.

Example 1: $ZnZrF_6 \cdot 6H_2O$

The Pauling's radii are $r_{Zn^{2+}} = 0.74$ Å, $r_{Zr^{4+}} = 0.80$ Å, $r_{F^-} = 1.33$ Å, and $r_{O^{2-}} = 1.40$ Å. The sizes of cations as well as the sizes of anions are very close. The coordination number for both cations with every one of the ligands is six. Consequently the structure must be formed by two kinds of octahedra, around Zn^{2+} and around Zr^{4+}. The composition of these octahedra, i.e., the kind and the number of ligands around the respective metal ion, will be determined using the χ-factor. The possible metal–ligand combinations give the following values of χ:

Zn–F	$\chi = -3.24$
$Zn–H_2O$	$\chi = -1.76$
Zr–F	$\chi = 28.84$
$Zr–H_2O$	$\chi = 15.69.$

If the structure consists of the complexes $Zn(H_2O)_6$ and ZrF_6, the total χ value will be $\chi = 6\chi_{Zn-H_2O} + 6\chi_{Zr-F} = 162.48$.

If the complexes are ZnF_6 and $Zr(H_2O)_6$, the total $\chi = 74.70$. Intermediate combinations, i.e., structures $[Zn(H_2O)_kF_{6-k}]$ $[Zr(H_2O)_{6-k}F_k]$, where k is from 1 to 5, give values of χ between 74.70 and 162.48. As we know, the first combination of complexes exists in $ZnZrF_6 \cdot 6H_2O$ and the χ value is highest for it.

Example 2: $CdMg_2Cl_6 \cdot 12H_2O$

The combination of two $Mg(H_2O)_6$ and one $CdCl_6$ octahedra yields $\chi = 65.70$. At the other extreme, if Mg^{2+} coordinates with six Cl^- and Cd^{2+} with six H_2O, then the remaining six H_2O molecules must surround the second Mg^{2+}. This combination $[MgCl_6][Mg(H_2O)_6][Cd(H_2O)_6]$ gives $\chi = 19.38$. The structure contains the first combination of complexes for which χ is higher.

Example 3: The structure of $CaMg_2Br_6 \cdot 12H_2O$ is unknown

The probable possibilities are between $[Mg(H_2O)_6]_2[CaBr_6]$ and $[Ca(H_2O)_6][MgBr_6][Mg(H_2O)_6]$. For the first case, $\chi = 55.62$ and for the second, $\chi = 53.82$. The χ-values for the intermediate structures lies between 55.62 and 53.82. It appears that the structure $[Mg(H_2O)_6]_2[CaBr_6]$ is the most probable since χ is the highest for it. Taking into account that the respective chloride and bromide hydrates of Ca and Mg are isostructural, we expected (*4*) this salt to be isostructural with $CaMg_2Cl_6 \cdot 12H_2O$. Our calculations now confirm this assumption.

The χ-factor gives some other possibilities. For instance, it allows one to compare the stabilities of structures of double salts of the same type when different ligands are substituted.

Example 4: Formula type $CaMg_2X_6 \cdot 12H_2O$ (X = Cl,Br,I)

Assuming that these structures are formed by the complexes $[Mg(H_2O)_6]_2$ $[CaX_6]$, the values of χ will be $CaMg_2Cl_6 \cdot 12H_2O$ ($\chi = 65.70$), $CaMg_2Br_6 \cdot 12H_2O$ ($\chi = 55.62$), $CaMg_2I_6 \cdot 12H_2O$ ($\chi = 42.90$).

The value of χ decreases in going from Cl to I, so that we can say that the structure of $CaMg_2Cl_6 \cdot 12H_2O$ is more stable than $CaMg_2Br_6 \cdot 12H_2O$ on equal terms. Proof of this conclusion is that the double salt $CaMg_2Cl_6 \cdot 12H_2O$ appears in the ternary $CaCl_2–MgCl_2–H_2O$ system at 25°C (*5, 6*) and it possesses a rather wide crystallization field at 35 and 75°C (*7*). On the other hand, in the $CaBr_2–MgBr_2–H_2O$ system (*4*) there is no double salt at 25°C and $CaMg_2Br_6 \cdot 12H_2O$ appears at 50°C but with a very narrow crystallization field. According to Van't Hoff (*8*), all three double salts considered must extend their crystallization fields when the temperature rises. As for the iodide salt, $CaMg_2I_6 \cdot 12H_2O$, its χ value is the smallest. Consequently this double salt must appear at a still higher temperature in the respective ternary system. In our view, this kind of comparison of structure stabilities is reliable only in the cases of formation of double salts of the same type and of the same number in their respective ternary systems.

Example 5: In the $MnCl_2$–$ZnCl_2$–H_2O system at 25°C there is no double salt formation (*9*)

A relationship was found in our earlier papers (*10, 11*) that double salts in MeL_2–MeL_2–H_2O systems are formed when both metal ions, or at least one of them, are d^5 (high-spin state), d^{10}, or p^6 ions, i.e., their crystal field stabilization energy is zero. These configurations allow strong angular deformation of the coordination polyhedra and favor the double salt formation. The relationship was reported first for chloride systems (*10*) and was confirmed for acetate (*11*) and bromide (*4, 39*) systems. Since Mn^{2+} is a d^5 high-spin state ion and Zn^{2+} is a d^{10} ion, a double salt should form in the $MnCl_2$–$ZnCl_2$–H_2O system. In the system $MnBr_2$–$ZnBr_2$–H_2O we found (*12*) the double salt $MnBr_2 \cdot ZnBr_2 \cdot 6H_2O$ at 25°C. Taking into account the hardness values of cations and ligands and the ability of Zn^{2+} to form tetrahedral halogenide complexes, the most reliable complex structure of this double salt is $[Mn(H_2O)_6][ZnBr_4]$. If one calculates the χ values for this combination for the chloride and bromide structures, it is seen that the bromide salt ($\chi = 6.26$) is more stable than the chloride salt ($\chi = 1.38$). This explains the absence of the chloride salt in the respective ternary system at 25°C. In keeping with our conclusions and according to Van't Hoff's Rule (*8*), the chloride double salt is expected to appear at a lower temperature.

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