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STABILIZATION OF METAL COMPLEXES BY LARGE COUNTER-IONS

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INTRODUCTION

Science lends itself to various degrees of sophistication, and chemistry is no exception. Often it is the less sophisticated qualitative generalization that is of greater practical value. One such generalization in chemistry is that similar substances interact with each other to a greater extent giving a more stable system than do dissimilar substances. This is a well known phenomenon and many different types of examples can be cited to support it. For instance, polar compounds dissolve in polar solvent, whereas non-polar compounds dissolve in non-polar solvents. Similarly, like solvents are completely miscible, but unlike solvents may be immiscible. This type of behavior is of common occurrence in chemistry as in life and is adaquately described by the proverb "birds of a feather flock together."

Such a truism, amply supported by experimental fact was referred to as *symbiosis* by Jørgensen[1]. This is the mutual stabilizing effect on metal complexes observed for systems containing either a flock of soft ligands or a flock of hard ligands[2]. Thus, $[Co(NH_3)_5X]^{2+}$ is far better bound for X = F than I, whereas $[Co(CN)_5X]^{3-}$ is most stable with X = I and not even known for X = F. This is in accord with NH_3 being a hard base and symbiosis favoring the hard F^- over soft I^-, but CN^- is soft so for the cyanide system the preference is for I^-. Similarly CO substitution of $Cr(CO)_6$ is very slow compared with that for $Cr(CO)_4$bipy[3], presumably because the hexacarbonyl is more stable due to symbiosis.

Operationally, Berzelius was aware of the fact that certain metals occur on the earth's crust as oxides and others as sulfides. Approximately one hundred fifty years have elapsed and we now feel very certain that metals can be classified as class (a) and class (b) metals[4] or hard and soft Lewis acids, respectively. The class (a) or hard metals show a preference for halide ions in the order $F^- > Cl^- > Br^- > I^-$, whereas the reverse order is found for the class (b) or soft metals. Pearson[5] has cleverly pointed out that such an approach can also be extended to organic systems, and he stated the general principle: *Hard acids prefer to associate with hard bases and soft acids prefer to associate with soft bases.*

The theme of this review is the importance of flocking together of like substances in chemical systems, and of particular interest here is the useful general principle: *Solid salts separate from aqueous solution easiest for combinations of either small cation—small anion or large cation—large anion, preferably with systems having the same but opposite charges on the counterions.* This is a well known fact to coordination chemists and others, but it needs to be emphasized because it is sometimes overlooked (see last section on errors).

Considering the general case represented by reaction (1),

$$C^{+}_{(aq)} + A^{-}_{(aq)} \rightleftharpoons C\,A_{(s)} \qquad (1)$$

it is seen that what determines whether or not the formation of solid compounds CA is favored is the difference between the hydration energies of the ions and the lattice energy of the solid. Clearly the driving force for the formation of the small cation–small anion system is the large lattice energy of CA, whereas for the large–large combination the driving force must be the small hydration energies of the large ions. This is illustrated by the values of the hydration energies of the ions and lattice energies of the solids in kcal/mole provided for the species in equations (2)–(5).

$$\begin{array}{lllcr}
 & & & \underline{\Delta H^{\circ}\text{, kcal/mole}} & (2)\\
Li^{+}_{(aq)} + & F^{-}_{(aq)} \rightleftharpoons & LiF_{(s)} & 0 & \\
-124 & -121 & -245 & & \\
Li^{+}_{(aq)} + & I^{-}_{(aq)} \rightleftharpoons & LiI_{(s)} & +16 & (3)\\
-124 & -70 & -178 & & \\
Cs^{+}_{(aq)} + & F^{-}_{(aq)} \rightleftharpoons & CsF_{(s)} & +14 & (4)\\
-66 & -121 & -173 & & \\
Cs^{+}_{(aq)} + & I^{-}_{(aq)} \rightleftharpoons & CsI_{(s)} & -5 & (5)\\
-66 & -70 & -141 & &
\end{array}$$

The results are in accord with the solids containing counter-ions of the small–small (LiF) and large–large (CsI) combinations being favored over the less similar systems LiI and CsF, respectively. In practice the facts support this, LiF is less soluble than LiI and CsI is less soluble than CsF. The importance of the same but opposite charges on the ions is shown by comparing the solubility of salts such as *$AgCl$*, Ag_2SO_4, Ag_3PO_4; $BaCl_2$, *$BaSO_4$*, $Ba_3(PO_4)_2$; $LaCl_3$, $La_2(SO_4)_3$, *$LaPO_4$*. For each metal ion its least soluble salt is in italics.

The importance of large ions stabilizing large counter-ions in the solid state is not restricted to reactions in aqueous solution, but is fairly commonplace also in other systems. For example, beginning students learn that although the alkali metals have very similar chemical properties, their reactions with oxygen are dramatically different. Lithium gives the expected oxide Li_2O, whereas cesium forms the superoxide CsO_2. This is said to result from the large Cs^+ having a greater stabilization effect on the larger O_2^- compared with the smaller O^{2-} relative to the reverse for the small Li^+. Beginning textbooks also often include the fact that the thermal stabilities of the alkaline earth carbonates increase in the order Mg_2CO_3

$< CaCO_3 < SrCO_3 < BaCO_3$, and attribute this to the stabilizing influence on the larger CO_3^{2-} relative to O^{2-} as the size of the cation increases from Mg^{2+} to Ba^{2+}.

Other textbook examples would include $M[ICl_4]$, where the stability of the solid increases for changes in M in the order Li < Na < K < Rb < Cs. Similarly for $R_4N[ICl_4]$, the stability of the salt increases with the increasing size of R_4N^+. More recent examples may include reactions (6) and (7)[6].

$$NaCl + BCl_3 \rightarrow \text{No reaction} \quad (6)$$

$$CsCl + BCl_3 \rightarrow Cs[BCl_4] \quad (7)$$

The isolation of Cd(I) as Cd_2^{2+} was achieved[7] by the stabilizing influence of $AlCl_4^-$ to give $Cd_2[AlCl_4]_2$.

Students (and also some faculty) are surprised to find that reaction (8) is exothermic.

$$\underset{-65}{LiI_{(s)}} + \underset{-127}{CsF_{(s)}} \rightarrow \underset{-146}{LiF_{(s)}} + \underset{-80}{CsI_{(s)}} \quad (8)$$

$$-65 \quad -127 \quad -146 \quad -80 = \Delta H_f \text{ kcal mole}$$

The heats of formation of the individual compounds are given and it is seen that the reaction is exothermic to the extent of 34 kcal/mole. We are conditioned to thinking that the combination of the most electropositive and most electronegative elements form the most stable compounds and, therefore, it is surprising to find that reaction (8) is not in the direction favoring the formation of CsF. Nature has its way and the small Li^+ small F^- plus large Cs^+ large I^- combinations are preferred over the reverse arrangement. This is due to the large lattice energy of LiF.

STABILIZATION OF METAL COMPLEXES

This section will refer to a few examples in which the metal complex in question is not stable in aqueous solution but is stable in the solid state. Keeping in mind that metal complexes are large in size, the previously stated principle can be restated as follows: *Solid metal complexes are stabilized by large counter-ions, preferably ions of the same but opposite charge*. Some of the large counter-ions that have been used for this purpose are shown in Table 1.

In the mid-fifties when crystal field theory appeared to be the answer to chemical bonding in metal complexes, it became of interest to isolate and characterize some tetrahedral nickel(II) complexes. This was achieved for $[NiCl_4]^{2-}$ and $[NiBr_4]^{2-}$ using the large cations $(C_2H_5)_4N^+$ and $(C_6H_5)_2CH_3As^+$ and ethanol as a solvent. The method of synthesis was readily applied to other analogous systems of the type $R_2[MX_4]$, where M^{II} = Mn, Fe, Co, or Zn and X = Cl, Br or I. In all of these cases the complexes $[MX_4]^{2-}$ are stable in ethanol solution at the conditions of these experiments.

are readily established. Thus $CuCl_5^{3-}$ is not stable in solution but it is produced in

TABLE 1

SOME LARGE COUNTER-IONS USED TO STABILIZE AND ISOLATE METAL COMPLEXES

Cations	*Anions*
Cs^+	ClO_4^-, I^-
R_4N^+	BF_4^-
$(C_6H_5)_4As^+$	PF_6^-
$(C_6H_5)_3CH_3As^+$	$AlCl_4^-$
$(C_6H_5)_4P^+$	$B(C_6H_5)_4^-$
$(C_6H_5)_3CH_3P^+$	$[Cr(NH_3)_2(NCS)_4]^-$
$[Co(NH_3)_4(NO_2)_2]^+$	$[Co(NH_3)_2(NO_2)_4]^-$
Ba^{2+}, $[Pt(NH_3)_4]^{2+}$	SiF_6^{2-}
$[Ni(phen)_3]^{2+}$	MCl_4^{2-} M = Co, Ni, Zn, Cd, Hg, Pt
$[Ni(bipy)_3]^{2+}$	$PtCl_6^{2-}$
$[Co(NH_3)_5NO_2]^{2+}$	$Fe(CN)_6^{2-}$
La^{3+}	$M(CN)_6^{3-}$ M = Fe, Co, Cr
$[M(NH_3)_6]^{3+}$ M = Co, Cr, Rh	$[M(C_2O_4)_3]^{3-}$ M = Co, Cr
$[M(en)_3]^{3+}$ M = Co, Cr, Rh	MF_6^{3-} M = Al, Fe, Co
$[M(pn)_3]^{3+}$ M = Co, Cr, Rh	
Th^{4+}	$[M(CN)_8]^{4-}$ M = Mo, W
$[Pt(NH_3)_6]^{4+}$	
$[Pt(en)_3]^{4+}$	

In contrast to this, the species $[CuCl_5]^{3-}$ can be isolated[9] from an aqueous solution that contains "none" of it by the addition of the cation $[Cr(NH_3)_6]^{3+}$. Since Cu^{II} complexes are substitution labile, it follows that the equilibria represented by (9)

$$\begin{array}{l} CuCl_3^- \rightleftharpoons CuCl_4^{2-} \rightleftharpoons CuCl_5^{3-} \\ \qquad\qquad\qquad\qquad\quad \downarrow [Cr(NH_3)_6]^{3+} \\ \qquad\qquad\qquad\quad [Cr(NH_3)_6]\,[CuCl_5] \end{array} \tag{9}$$

aqueous solutions containing excess Cl^- because of the driving force for the formation of the stable solid $[Cr(NH_3)_6]$ $[CuCl_5]$. This is an excellent illustration of the importance that the charge of the counter-ion be the same but opposite to that of the complex one wishes to stabilize. Note that the concentrations of $CuCl^{3-}$ and $CuCl_4^{2-}$ in solution far exceed that of $CuCl_5^{3-}$, but it is the 3- anion that is preferentially stabilized and brought out of solution.

It had also been assumed that $CuCl_5^{3-}$ is crystallized from solution by $[dienH_3]^{3+}$ (dien = $NH_2C_2H_4NHC_2H_4NH_2$), but a very recent x-ray study[10] shows that the substance obtained is a double salt and should be formulated as $[dienH_3]Cl[CuCl_4]$. This suggests that better results are expected if the counter-ion has a compact spherical shape similar to that of the metal complex to be stabilized, visavis $[Cr(NH_3)_6]^{3+}$ and not $[dienH_3]^{3+}$ relative to $CuCl_5^{3-}$. The structure of $CuCl_5^{3-}$ was determined by x-rays to be trigonal bipyramidal[11] and the

Cu–Cl distances[12] are shorter for the axial (2.296 Å) than for the equatorial (2.391 Å) positions.

Much the same discussion as that above applies to the six-coordinated complexes $[MCl_6]^{3-}$, where M = Cr, Mn or Fe, which are not stable in aqueous solution but can be stabilized in a crystal lattice[13] with $[Co(pn)_3]^{3+}$. The addition of a concentrated HCl solution containing these metal ions readily yields the salts $[Co(pn)_3]\,[MCl_6]$. Because the reaction mixtures are strongly acidic, the choice of a 3+ counter-ion requires that it be a substitution inter metal ammine.

It has long been known that pale yellow solutions of $Ni(CN)_4{}^{2-}$ become an intense orange-red color upon the addition of excess CN^-. Investigations of these solutions have shown[14] that this is due to the formation of the species $Ni(CN)_5{}^{3-}$. However, it could not be isolated as the potassium salt, because evaporation of the orange-red solution yielded a mixture of $K_2Ni(CN)_4 + KCN$ in the solid phase. The complex $Ni(CN)_5{}^{3-}$ was stabilized and isolated[15] as the salts of $[Cr(NH_3)_6]^{3+}$ and $[Cr(en)_3]^{3+}$. It has also been found possible[16] to isolate $K_3Ni(CN)_5$ at −15°C, but it is not stable at room temperature. These results are summarized by scheme (10).

$$\begin{tikzcd}
{[Cr(en)_3]\,[Ni(CN)_5]\ \text{stable solid}} & \\
Ni(CN)_5{}^{3-} \arrow[u, "{[Cr(en)_3]^{3+}}"] \arrow[r, "{K^+,\text{Conc.}}"] \arrow[d, "{-15^\circ}"', "K^+"] & K_2Ni(CN)_4 + KCN \\
K_3Ni(CN)_5 \arrow[ur, "\text{R.T.}"] &
\end{tikzcd} \tag{10}$$

The corresponding Co^{III} ammines were not suitable due to their undergoing substitution reactions at the experimental conditions of high CN^- concentration. This may be caused by the presence of catalytic amounts of Co^{II} and/or base catalysis in the strongly alkaline solution[17]. Neither of these effects are as pronounced here for the Cr^{III} ammines. Attempts to isolate $[Cr(en)_3]\,[Co(CN)_5]$ have not yet been successful[18]. The addition of $[Cr(en)_3]^{3+}$ to a concentrated solution of $[Co(CN)_5]^{3-}$ results in an immediate color change from intense green to yellow-orange. This suggests that the water reaction[19] (11) has been catalyzed.

$$2Co(CN)_5{}^{3-} + H_2O \rightleftharpoons [HCo(CN)_5]^{3-} + [Co(CN)_5OH]^{3-} \tag{11}$$

It was recently reported[20] that further reaction takes place to generate $[Co(CN)_6]^{3-}$, and in support of this the salt $[Cr(en)_3]\,[Co(CN)_6]$ was isolated[18]. This is being repeated in other solvents and also attempts[21] are being made to stabilize $Pd(CN)_5{}^{3-}$, $Pt(CN)_5{}^{3-}$ and $Au(CN)_5{}^{2-}$.

The structure of $[Cr(en)_3]\,[Ni(CN)_5]1.5H_2O$ has been determined by x-rays[22] and of special interest is the structure of $Ni(CN)_5{}^{3-}$. Theoretical chemists were reluctant to predict its structure, but at the author's insistence some did, and the predictions were 50% trigonal bipyramidal and 50% tetragonal pyramidal. Nature is on their side, for it is found that the symmetry cell contains two cations and two anions, one $Ni(CN)_5{}^{3-}$ is a tetragonal pyramid and the other is a distorted trigonal bipyramid. This means that the energy differences between the two structures must indeed be small[23]. Again the Ni-C bond distances in the axial positions are shorter than in the equatorial positions of the trigonal bipyramid. It begins to appear that this may be true for d^n systems where n is sufficiently large, whereas the reverse holds for d^o compounds[24].

Substitution reactions of tetrahedral Si^{IV} are generally bimolecular displacements which are believed to proceed through a five-coordinated active intermediate[25]. Silicon chemists were very pleased a few years ago when the stable five-coordinated Si^{IV} cation $[(C_6H_5)_3Si(bipy)]^+$ was isolated[26] as the I^-salt. It now appears that this previously illusive coordination number for Si^{IV} is readily obtained if one makes the proper choice of system and counter-ion. Thus $SiF_5{}^-$ is stabilized by $(C_6H_5)_4As^+$ and the salt separates from an aqueous-methanol solution of a reaction mixture represented by (12)[27].

$$SiO_2+5HF+(C_6H_5)_4AsCl \rightarrow (C_6H_5)_4AsSiF_5+HCl+2H_2O \qquad (12)$$

This synthesis was prompted by the x-ray studies which suggested the presence of $SiF_5{}^-$ in a substance previously incorrectly formulated (see last section).

In addition to qualitative experimental observations of the type mentioned above, quantitative thermodynamic data are also available which support the principle that a large counter-ion stabilized a metal complex. Some such data are shown in Table 2. The results clearly show that the stabilities of $AlH_4{}^-$ and of $VF_6{}^-$ increase for the respective salts in the order Li < Na < K < Rb < Cs.

TABLE 2

THERMODYNAMIC DATA SHOWING THE INCREASE IN STABILIZATION OF METAL COMPLEXES WITH INCREASE IN SIZE OF COUNTER-ION

$MAlH_4{}^a{}_{(s)} \rightarrow MH_{(s)}+Al_{(s)}+3/2H_{2(g)}$					
	Li	Na	K	Cs	
ΔG^o, kcal/mole	−3.9	+3.0	+14.9	+16.5	
$MVF_6{}^b{}_{(s)} \rightarrow MF_{(s)}+VF_{5(s)}$					
	Li	Na	K	Rb	Cs
ΔG^o, kcal/mole	−55	−25	+1	+7	+14

[a] Ref. 28. [b] Ref. 29.

ISOLATION OF METAL COMPLEXES

Not as spectacular as some of the examples mentioned in the previous section, but perhaps even of greater importance to the coordination chemist is the proper choice of counter ion to permit the isolation of a metal complex that is stable in solution (so much so that most of its salts are extremely soluble and difficult to isolate). A past master at being able to isolate systems difficult to obtain was the late Professor Dwyer[30]. It has been said that if he could not resolve a metal complex then it must not be optically active. His approach was simply that of using with his gifted "green thumb", appropriate counter-ions of large size and the same but opposite charge. For example, he was able to start with (+)–$[Co(en)_2(NO_2)_2]^+$ and resolve several other Co^{III} complexes as represented by scheme (13).

$$\begin{array}{lll} & \nearrow & (+)\text{-}[Co(EDTA)]^- \rightarrow (+)\text{-}[Co(en)_2C_2O_4]^+ \\ (+)\text{-}[Co(en)_2(NO_2)_2]^+ & \rightarrow & (+)\text{-}[Co(en)(C_2O_4)_2]^- \rightarrow (+)\text{-}[Co(en)_2CO_3]^+ \\ & \searrow & (-)\text{-}[Co(en)(mal)_2]^- \end{array} \qquad (13)$$

Some of these complexes such as $[Co(EDTA)]^-$ had been previously resolved[31] but were not obtained optically pure until the proper choice of resolving agent was made.[32]

Aquo complexes often form very easily in water solution, but their isolation may not be easy because of their extreme solubility. For example this is true of *cis*-$[Cr(en)_2(H_2O)Cl]^{2+}$. However, it is possible to isolate this complex as the salt *cis*-$[Cr(en)_2(H_2O)Cl]ZnCl_4$ (or $ZnBr_4$) from an aqueous ethanol solution[33]. Similarly, the salt $[Co(tetraen)Cl]Cl_2$ is very soluble and when it was first prepared no attempt was made to separate its various geometrical isomers[34]. The α and β forms of this complex have now been obtained[35] as the salts of $ZnCl_4{}^{2-}$.

Many cationic and anionic metal carbonyls and their derivatives have been prepared and often their isolation is accomplished with a large counter-ion of the same but opposite charge. This is best illustrated by reaction (14).

$$Mn(CO)_5Cl + CO + AlCl_3 \rightarrow [Mn(CO)_6]AlCl_4 \qquad (14)$$

In this instance the investigators[36] were doubly fortunate since the Lewis acid required to remove the chloro group from $Mn(CO)_5Cl$ was also able to provide the necessary anion for the formation of a stable salt with the cation $[Mn(CO)_6]^+$. A few other examples with references but no comment are $R_4N[Mn(CO)_4X_2]$[37], $R_4N[Cr(CO)_5X]$[38], $R_4N[Rh(CO)_2X_2]$[39], $[Cr(Triars)(CO)_2X]B(C_6H_5)_4$[40], $[C_5H_5Cr(CO)_4]Br_4$[41], $[C_5H_5Fe(CO)_3]PF_6$[42].

ERRORS

Mistakes have been made because investigators have failed to give enough credence to the phenomenon that large counterions stabilize metal complexes. This author[43] is guilty of such an error and can use his naivete at the time as the first example. At the early stages of our investigations on the mechanisms of substitution reactions of metal complexes, it was of interest to design an experiment to determine if water is involved in a nucleophilic displacement process for aquation reactions of Co^{III} complexes (incidently, it is still of interest to design such an experiment.)[17]. For this purpose a series of complexes of the type *trans*-$[Co(AA)_2Cl_2]^+$ were prepared, where AA = C- and N-alkyl substituted ethylenediamines. The compounds were prepared by the method used to prepare the well known *trans*-$[Co(en)_2Cl_2]Cl$ and the results obtained were similar to those described for this compound. All of the compounds were green and had visible absorption spectra similar to that of *trans*-$[Co(en)_2Cl_2]^+$. This complex separates from its reaction mixture as *trans*-$[Co(en)_2Cl_2]Cl.\ 2H_2O.HCl$[44], but the H_2O-HCl can be removed by heating it in an oven at 110° overnight. It was assumed that HCl was more difficult to remove from the substituted- en complexes, because even after heating for longer periods they still gave high chlorine analyses. The complexes were incorrectly formulated as *trans*-$[Co(AA)_2Cl_2]Cl.nHCl$. Recent studies show that the compounds were instead *trans*-$[Col(AA)_2Cl_2]_2CoCl_4$[45]. Lest someone gets overly concerned as to the validity of the aquation studies, these were performed with the pure ClO_4^- salts.

A very recent example of the mistaken identity of a compound due to failure to heed the essential theme presented here, is provided by the reaction of *trans*-$[Pt(PEt_3)_2HCl]$ with C_2F_4 in cyclohexane solution in a glass vessel at 120° for 50 hr. One of the minor products, obtained in about 10% yield, was formulated[46] as $[Pt(PEt_3)_2(H)\ (Cl)\ (C_2F_4)]$. It was claimed that this formula was supported by its analysis (Pt, P, F – not C, H although C and H analyses were reported for the other products), its ir spectrum and its ^{19}F nmr spectrum. Although conductivity measurements in nitrobenzene showed the compound to be a 1:1 electrolyte, this was suggested to involve a dissociation of a H^+ or a Cl^-. The formula proposed for this substance seemed plausible on the basis of the available evidence, but even more so because such a compound is believed to be the active intermediate leading to the overall insertion (or ligand migration)[17] reaction to form the sigma bonded alkyl product.

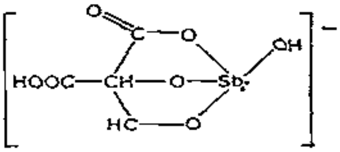
A sample of the compound was examined by means of x-rays and it was quickly determined that it contained two aggregates, presumably a cation and an anion in keeping with its being a 1:1 electrolyte. It was also impossible to find C_2F_4 in the compound. The research group at Northwestern University[47] began to speculate that the ir band at 2100 cm.$^{-1}$ which had been assigned to Pt-H stretch was in fact due to C–O stretch and that the cation may be $[Pt(PEt_3)_2COCl]^+$ which is isoelectronic with the Vaska Ir^I compound. The anion had a regular tetrahedral structure, and it appeared this could be BF_4^- coming from the reaction of the Pyrex glass tube with HF. Also contained in this preparation was the anion SiF_5^-, which is the only anion when the preparation is carried out in silica tubes.

The correct formula for this compound, *trans*-$[Pt(PEt_3)_2COCl]BF_4$ (or SiF_5) is in accord with the large anion stabilization of the complex and agrees with its properties as previously reported. The final confirmation of this structure is the rational synthesis of the BF_4^- salt by the research group at the University of

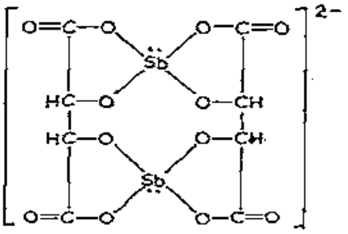
Western Ontario. The compound *trans*-[Pt(PEt$_3$)$_2$HCl] reacts with CO and aqueous HBF$_4$ under pressure to yield *trans*-[Pt(PEt$_3$)$_2$COCl]BF$_4$. In addition the rational synthesis of (C$_6$H$_5$)$_4$AsSiF$_5$ was accomplished as shown by reaction (12). Further studies are in progress on the syntheses and reactions of these systems[48].

Often the (+)-tartrate ion is not a suitable resolving agent for metal complexes, and some years ago it was found that better results may be obtained using antimonyl (+)-tartrate ion[49]. It appeared that this worked best with 2+ cations such as [Ni(bipy)$_3$]$^{2+}$ and [Fe(phen)$_3$]$^{2+}$, which would be contrary to the same but opposite sign on the anion if it is correctly formulated as (+)-[SbO(C$_4$H$_4$O$_6$)]$^-$. The recent important synthesis and resolution[50] of *cis*-[Pt(en)$_2$Cl$_2$]$^{2+}$ made use of the diastereoisomeric salt (+)^{450}-*cis*-[Pt(en)$_2$Cl$_2$]-(+)-[ShO(C$_4$H$_4$O$_6$)]$_2$.

The x-ray structure determination of K[SbC$_4$H$_4$O$_7$].1/2H$_2$O shows the anion to be

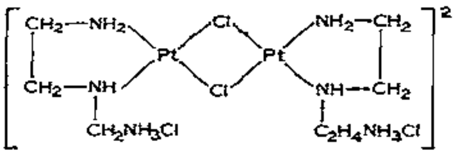


with a distorted tetrahedral structure around antimony[51]. Recent x-ray studies[52] on (+)-[Fe(phen)$_3$] [(+)-SbC$_4$H$_4$O$_7$]$_2$ affords the most "expected" result that the anion indeed has a 2− charge.



The structure at antimony is that of a distorted tetrahedron, and the absolute configuration of [Fe(phen)$_3$]$^{2+}$ was determined.

Finally, the reaction of K$_2$PtCl$_4$ with dien.3HCl yielded a pale yellow crystalline product which was assigned[53] the empirical formula PtC$_8$H$_{30}$ON$_6$Cl$_8$, perhaps as a typographical error because the analytical data reported require Pt$_3$C$_8$H$_{30}$ON$_6$Cl$_8$. In any case no attempt was made to designate the structure of this species. Recent detailed studies[54] of this system show it to be [Pt$_2$C$_8$H$_{28}$N$_6$Cl$_2$]PtCl$_4$.H$_2$O and that the cation has the structure



This provides yet another example of a large cation being stabilized by a large anion of the same but opposite charge.

In conclusion it need only be said that if the reader still remains skeptical of the importance and practical value of the general principle discussed here, then he is referred to the chemical literature which abounds with many more examples, some of which may better suit his fancy.

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