Comparative Chelate Stabilities By Potentiometric Titrations

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COMPARATIVE CHELATE STABILITIES
BY POTENTIOMETRIC TITRATIONS

by
Jamee B. Smart

A Dissertation
Submitted to the
Department of Chemistry
of
Carroll College

In Partial Fulfillment
Of the Requirements
For the Degree of
B. A. With Honors

May 1, 1959
Approved by: James A. Ryan
May 5, 1959
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A chelate is a particular type of a complex or coordination compound. When a metal ion occupies two or more places on an electron donor to form a ring, it is said to form a chelation compound, the electron donor being considered the chelating agent. The word "chelate", applied to such a structure, comes from the Greek "chele", meaning claw, and thus ligands (or chelating agents) are said to be bidentate, tridentate, quadridentate, (two teeth, three teeth, four teeth, etc.) depending on the number of atoms open on the ligand for chelation.

Complexes and chelates are formed by nearly all of the metals of the periodic system. Although the number of known chelating and complexing agents is very large, the donor atoms which undergo combination with the metal are restricted to the strongly non-metallic elements of Groups V and VI. Of these, N, O, and S are the only common examples (1).

The number of applications which man has found for this class of compounds is remarkable. However, man cannot take credit for the two most important uses of chelate compounds; the use of the magnesium chelate, chorophyll, as a catalyst for the incorporation of the hydrogen of water into plant systems; and the use of the iron chelate, heme, as an oxygen carrier in human respiration. Chelates have found use as textile dyes, bacteriacides, water softeners, enzyme deactivators, or artificial "oxygen-carriers". They are used for approximate colorimetric estimation of ions in analytical chemistry, and they have proven valuable in separating metal ions by solvent extraction (2).

Perhaps the most important division of research in chelate chemistry today is the correlation of data concerning the relative stabilities of
the various chelates with their composition and structure. Attempts have been made to fit cations into a series in order of their "tendency toward coordination", but have met with little success, as the order depends to some extent upon the chelating agent used as reference base. The most common is the Mallor and Maley series, based upon a limited number of divalent ions as listed below according to decreasing "electrophilic character". One is perhaps tempted to link this order with the order of the second ionization potentials (listed below the elements), but lead, zinc, and palladium are out of place.

<table>
<thead>
<tr>
<th>Ion</th>
<th>2nd IP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd++</td>
<td>19.8</td>
</tr>
<tr>
<td>Cu++</td>
<td>20.2</td>
</tr>
<tr>
<td>Ni**</td>
<td>18.2</td>
</tr>
<tr>
<td>Pb++</td>
<td>15.0</td>
</tr>
<tr>
<td>Co++</td>
<td>17.3</td>
</tr>
<tr>
<td>Zn++</td>
<td>17.9</td>
</tr>
<tr>
<td>Cd++</td>
<td>16.8</td>
</tr>
<tr>
<td>Fe++</td>
<td>16.2</td>
</tr>
<tr>
<td>Mn++</td>
<td>15.7</td>
</tr>
<tr>
<td>Mg++</td>
<td>15.0</td>
</tr>
</tbody>
</table>

It should be remembered that this is not a fixed pattern, but a general one. Another general rule, for a series of ions having the same charge, is that the smaller ions tend to form more stable complexes than the larger (3).

There is another important factor in the study of chelate stabilities and that is of the structure of the chelate itself. It has been found that if in the coordinate ring there are alternating double bonds, thus giving a resonance effect and spreading the pi-electron density over the ring, the chelate is often more stable, and in some cases it can mean the difference between forming a chelate and no chelate at all (4).

This study will not involve the effect of the immediate chelation ring, but upon a ring in conjunction with the chelating ring. That is, we shall first study the stabilities of a known chelating compound, o-nitrobenzoic acid, (5), with various cations, and then studying the stability of a similar ligand, 3,5, dinitrobenzoic acid, with these same cations, and comparing the results. The reason for the selection of the
latter compound for the comparison is the effect of the added nitro group upon the resonance of the benzene ring. The effect of this nitro group upon the resonance of benzene and the inductive effect according to Møller (6), operate in the same direction and cause increased acidity when in either the meta or para position. Two nitro groups in the ortho or para positions give an acid approximately as strong as carboxylic acid, since this resonance effect (interaction of the pi-orbitals) decreases the electron density on the oxygen atom and permits loss of a proton more easily. In general, the resonance effects are more important than the inductive effects, but for the nitro group the inductive and resonance effects are in the same direction. This would seem to indicate that 3,5 dinitrobenzoic acid would form the strongest acid of the two (that is, would be the better proton donor of the two), however, in aqueous solutions this is not true (7) (K for o-nitrobenzoic acid = 6.71 x 10^-3, while K for 3,5 dinitrobenzoic acid = 1.63 x 10^-3). But again, in a 50% alcohol (ethyl) solution, the 3,5 dinitrobenzoic acid did form the stronger acid (see graph I). On the onset of this experiment, this might also indicate that 3,5 dinitrobenzoic acid, being the strongest proton donor (in these circumstances) would also be the better chelating agent (that is, form the strongest chelation compounds). This is the assumption that led to the use of this compound for the comparison.

It might also be of interest to note here the deviation from the above Møller - Maley series, especially of the Zn^{++} cation.
3,5 dinitrobensoic acids were both used as obtained from Eastman Kodak, and were dissolved in the 50% alcohol-water solution of 0.01584 N HClO₄ to give 3.9 meq. per 100 ml.; the cations Cd⁺⁺, Ni⁺⁺, Zn⁺⁺, Co⁺⁺, and Pb⁺⁺ were obtained from their nitrate salts and used in the above solutions at 10⁻⁴ molar. The 0.140 N NaOH was stored in a wax-lined bottle, with all entrances to the bottle protected by calcium chloride tubes filled with NaOH pellets. The liquid was forced out of the bottle by CO₂ free air.

PROCEDURE
Firstly, 100 ml of the 50% alcohol-water solution of 0.01584 N HClO₄ was titrated with the 0.140 N NaOH and the curve determined, then 100 ml of the acid solution with 3.9 meq. of the chelate added and curves (two) determined, (see graph I.), and finally 100 ml of the acid, with 3.9 meq. of chelating agent and 10⁻⁴ molar cation concentration. The titrations were carried out by adding a measured amount of NaOH from the micro-buret in such amounts as to keep the pH changing approximately 0.2 per addition. All titrations were carried out in a 50% alcohol-water solution of 0.01584 N HClO₄.
Graph I.

- 3.9 meg o-nitrobenzoic acid in HClO₄
- 3.9 meg 3,5 dinitrobenzoic acid in HClO₄
- 0.015 84 N HClO₄
Graph II.

α - o-nitrobenzoic acid

ε - Cd** in o-nitrobenzoic acid

γ - Cd* in 3,5 dinitrobenzoic acid

β - 3,5 dinitrobenzoic acid
Graph III.

\[ \text{\(\alpha\)-o-nitrobenzoic acid} \]
\[ \text{\(\beta\)-Ni}^+ \text{ in o-nitrobenzoic acid} \]
\[ \text{\(\gamma\)-Ni}^+ \text{ in 3,5 dinitro benzoic acid} \]
\[ \text{\(\delta\)-3,5 dinitrobenzoic acid} \]
Graph IV.

a. o-nitrobenzoic acid
b. Zn⁺ in o-nitrobenzoic acid
c. 3,5-dinitrobenzoic acid

Zn⁺ in 3,5-dinitrobenzoic acid.
Graph V.

α - o-nitrobenzoic acid
β - Co" in o-nitrobenzoic acid
γ - Co" in 3,5 dinitrobenzoic acid
δ - 3,5 dinitrobenzoic acid
Graph VI

a- o-nitrobenzoic acid
b- Pb in o-nitrobenzoic acid
c- 3,5 dinitrobenzoic acid
d- Pb in 3,5 dinitrobenzoic acid.

ml of base added
<table>
<thead>
<tr>
<th>ION</th>
<th>CHELATE</th>
<th>excess NaOH needed in ml. x 10^-1 at pH of:</th>
<th>H⁺ released by metal in M/l x 10^-2 at pH of:</th>
<th>Refer to Graph</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3.40</td>
<td>4.00</td>
<td>4.80</td>
</tr>
<tr>
<td>Cd++]</td>
<td>o-nitrobenzoic acid</td>
<td>1.5</td>
<td>-0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>3,5 dinitrobenzoic acid</td>
<td>-1.8</td>
<td>-1.6</td>
<td>-2.2</td>
</tr>
<tr>
<td>Ni++]</td>
<td>o-nitrobenzoic acid</td>
<td>2.6</td>
<td>2.1</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>3,5 dinitrobenzoic acid</td>
<td>0</td>
<td>0</td>
<td>0.4</td>
</tr>
<tr>
<td>Zn++]</td>
<td>o-nitrobenzoic acid</td>
<td>11.7</td>
<td>5.4</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>3,5 dinitrobenzoic acid</td>
<td>4.8</td>
<td>4.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Co++]</td>
<td>o-nitrobenzoic acid</td>
<td>5.4</td>
<td>5.0</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>3,5 dinitrobenzoic acid</td>
<td>-0.9</td>
<td>-1.3</td>
<td>-2.1</td>
</tr>
<tr>
<td>Pb++]</td>
<td>o-nitrobenzoic acid</td>
<td>4.8</td>
<td>3.5</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>3,5 dinitrobenzoic acid</td>
<td>3.8</td>
<td>2.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>
EXPLANATION OF GRAPHS AND DATA TABLE:

Graph:

The pH is plotted versus the ml of NaOH added. The dotted lines represent the respective chelate titrated without the metal, whereas the solid lines represent the chelate with metal titration. All titrations were done in a 50% alcohol water solution of 0.01584 M HClO₄. The NaOH used for the titrations was 0.140 N.

Table:

Each ion used is listed with both chelating agents, separated by a dashed line (horizontal). At the head of each column, is listed the pH at which the set of data following were tabulated. The first three columns represent the excess base needed, in ml x 10⁻¹, to compensate for the difference between the chelate without metal and the chelate with metal titrations, or the amount of base needed to neutralize the excess H⁺ ion caused by the chelation at that pH. The second three represent the amount of H⁺ equivalent to the amount of base used in the preceding three columns, or, the amount of H⁺ liberated at that pH, in M/l x 10⁻².

CONCLUSION:

By comparison of the data compiled in the table and the titration curves on the graphs, it is definitely indicated that 3,5 dinitrobeneolic acid is not as strong a chelating agent as is o-nitrobenzoic acid. It is also observed that the NO₂ in the three position of the benzene ring has a definite effect on the chelation, in this case a retarding effect.
It would be interesting here to note that although the 3,5 dinitrobenzoic acid was the strongest acid in the alcohol solution, that o-nitrobenzoic acid with the larger dissociation constant was the better chelating agent. Also, in the case of Cadmium and Cobalt where there was a very weak chelate formed with o-nitrobenzoic, the metal ion appeared to cause repression of the $H^+$ ion with 3,5 dinitrobenzoic, however an explanation of this is not immediately apparent.

It is not the purpose of this thesis to explain this phenomenon of the retardation by the extra NO$_2$ group, but theories might be put forth. First, it might be supposed that the increased symmetry of the molecule might tend to introduce the factor of steric hindrance; and secondly, the increased negativity close to the NO$_2$ groups might be great enough to compete, to some degree, for the incoming positive metal ion. That is, perhaps the compound also chelates to some extent with the two NO$_2$ groups, or the NO$_2$ groups are both competing for the open bond not occupied by the acid oxygen, in either case weakening the whole complex.

In any case, the additional NO$_2$ group showed a weakening of this particular type of molecule for chelation.
Reference list:

(1) Martell and Calvin, "Chemistry of Metal Chelate Compounds". Page 1

(2) Gould, "Inorganic Reactions and Structures". Pages 337-338

(3) Gould, "Inorganic Reactions and Structures". Pages 335-336

(4) Gould, "Inorganic Reactions and Structures". Page 337
& Martell and Calvin, "Chemistry of Metal Chelate Compounds". Pages 160-162

(5) Martell and Calvin, "Chemistry of Metal Chelate Compounds". Page 545

(6) Noller, "Chemistry of Organic Compounds". Pages 548-549, 503, 478, 504

(7) Hailgrown, "Dictionary of Organic Compounds".