Transition Metal Behavior and Analysis of Potential Complexation, Chelation

Abstract: The behavior of transition metal ion solutions (and a solution involving aluminum) is observed during the addition of basic solutions (sodium hydroxide, ammonia), and one chelating compound, glycine. Color changes in combination with the degree of precipitation, if any, are observed as an indication of the relative degree of complexation, and in the case of glycine, chelation of the metal ions.

Introduction:

Nine metal ion solutions of 0.2M concentration are measured into transparent glass beakers in equal volumes of 1.0 mL each: Aluminum Nitrate, Chromic Nitrate, Cobaltous Nitrate, Ferric Chloride, Ferrous Sulfate, Zinc Nitrate, Nickel Nitrate, Cupric Nitrate, and Manganous Chloride. Three sets of these beakers are set up so that each set can be observed interacting with a 0.6M solution of either sodium hydroxide, ammonia, or glycine. In the case of the first two, these solutions are first added in increments of a minimum volume (see method section) so that any insoluble precipitate that forms indicates a control volume of that base that should be expected to precipitate identical metal ions if they should remain in the beaker set to which glycine has been added. In the case of the glycine set, additions to each beaker are incremental by 0.33 mL so that a one-to-one or other integer ratio of glycine to metallic ions is maintained. This ratio and its correspondence to observations of color change and/or precipitation is the basis for analysis of complex ion stoichiometry as presented in results: if a complex forms in any beaker, a color change in the fraction of clear solution in the beaker may be noted; if a precipitate forms only, then there is no evidence of complexation. Reactions that produce precipitates in the above metallic ion solutions follow.

\begin{align*}
\text{Al(NO}_3\text{)}_3 \text{(aq)} + 3\text{NaOH (aq)} & \rightarrow \text{Al(OH)}_3 \text{(s)} + 3\text{NaNO}_3 \text{(aq)} & \text{[Equation 1.]} \\
\text{Cr(NO}_3\text{)}_3 + 3\text{NaOH (aq)} & \rightarrow \text{Cr(OH)}_3 \text{(s)} + 3\text{NaNO}_3 \text{(aq)} & \text{[Equation 2.]} \\
\text{Co(NO}_3\text{)}_2 + 2\text{NaOH (aq)} & \rightarrow \text{Co(OH)}_2 \text{(s)} + 2\text{NaNO}_3 \text{(aq)} & \text{[Equation 3.]} \\
\text{FeCl}_3 + 3\text{NaOH (aq)} & \rightarrow \text{Fe(OH)}_3 \text{(s)} + 3\text{NaCl (aq)} & \text{[Equation 4.]} \\
\text{FeSO}_4 + 2\text{NaOH (aq)} & \rightarrow \text{Fe(OH)}_2 \text{(s)} + 2\text{NaSO}_4 \text{(aq)} & \text{[Equation 5.]} \\
\text{Zn(NO}_3\text{)}_2 + 2\text{NaOH (aq)} & \rightarrow \text{Zn(OH)}_2 \text{(s)} + 2\text{NaNO}_3 \text{(aq)} & \text{[Equation 6.]} \\
\text{Ni(NO}_3\text{)}_2 + 2\text{NaOH (aq)} & \rightarrow \text{Ni(OH)}_2 \text{(s)} + 2\text{NaNO}_3 \text{(aq)} & \text{[Equation 7.]} \\
\text{Cu(NO}_3\text{)}_2 + 2\text{NaOH (aq)} & \rightarrow \text{Cu(OH)}_2 \text{(s)} + 2\text{NaNO}_3 \text{(aq)} & \text{[Equation 8.]} \\
\text{MnCl}_2 + 2\text{NaOH (aq)} & \rightarrow \text{Mn(OH)}_2 \text{(s)} + 2\text{NaCl (aq)} & \text{[Equation 9.]} \\
\end{align*}

In the case of ammonia, the following reactions are possible given a high enough hydroxide concentration in some cases where complexes more readily form:

\begin{align*}
\text{Al(NO}_3\text{)}_3 \text{(aq)} + 3\text{NH}_4\text{OH (aq)} & \rightarrow \text{Al(OH)}_3 \text{(s)} + 3\text{NaNO}_3 \text{(aq)} & \text{[Equation 10.]} \\
\text{Cr(NO}_3\text{)}_3 + 3\text{NH}_4\text{OH (aq)} & \rightarrow \text{Cr(OH)}_3 \text{(s)} + 3\text{NaNO}_3 \text{(aq)} & \text{[Equation 11.]} \\
\text{Co(NO}_3\text{)}_2 + 2\text{NH}_4\text{OH (aq)} & \rightarrow \text{Co(OH)}_2 \text{(s)} + 2\text{NH}_3\text{NO}_3 \text{(aq)} & \text{[Equation 12.]} \\
\text{FeCl}_3 + 3\text{NH}_4\text{OH (aq)} & \rightarrow \text{Fe(OH)}_3 \text{(s)} + 3\text{NH}_4\text{Cl (aq)} & \text{[Equation 13.]} \\
\end{align*}
Finally, the strength of chelation is tested in the glycine set by adding the control volume of sodium hydroxide and observing if any precipitate forms. If so, the precipitate indicates one of the above products has formed and chelation has most likely not occurred. Additional amounts of hydroxide allow for a determination of the relative ability of each chelated metal ion to remain chelated in a solution of increasing pH. More pertinent than pH per se is the hydroxide ion concentration or “strength”, a propos pH, that is required to precipitate the metal ion from the chelated complex solution.

Method:

Clear beakers are used so that observations are readily available. It was important to arrive at the smallest minimum volume measurable with 1 mL plastic pipettes. The second unlabeled mark from the tip of the beaker was used for this arbitrary minimum, the volume of which was determined by repeating a precise measurement to that mark ten times into a beaker before measuring that amount in the same pipette with regard to labeled metrics. This gave a volume of 0.72 mL and reflects the style of use peculiar to this experimenter.

Results:

(Continued on page 3.)
Table 1: Observations in Three Sets of Controlled Metal Ion Solutions upon Addition of NaOH, NH₄OH, and NH₂CH₂COOH

<table>
<thead>
<tr>
<th>Start</th>
<th>Al(NO₃)₃</th>
<th>Cr(NO₃)₃</th>
<th>Co(NO₃)₂</th>
<th>FeCl₃</th>
<th>FeSO₄</th>
<th>Zn(NO₃)₂</th>
<th>Ni(NO₃)₂</th>
<th>Cu(NO₃)₂</th>
<th>MnCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clear</td>
<td>Deep indigo-purple</td>
<td>Red-pink</td>
<td>Slightly cloudy orange</td>
<td>Bright yellow orange</td>
<td>Clear</td>
<td>Bright green</td>
<td>Bright light blue</td>
<td>Very slightly pink</td>
</tr>
<tr>
<td>1 mL in beaker (before any addition)</td>
<td>0.20 mL added, white gel/precipitate on contact</td>
<td>0.072 mL added, green precipitate on contact, dissolved to give more indigo solution</td>
<td>0.072 mL added, blue gel on contact does not dissolve when shaken</td>
<td>0.072 mL added, rust-colored gel on contact does not dissolve when shaken</td>
<td>0.072 mL added, dark green gel on contact does not dissolve when shaken</td>
<td>0.072 mL added, white gel formed, does not dissolve when shaken</td>
<td>0.072 mL added, light white or green gel precipitate, did not dissolve when shaken</td>
<td>0.072 mL added, dark blue chunks or gel formed</td>
<td>0.072 mL added, yellow-orange gel formed on contact</td>
</tr>
<tr>
<td>Upon addition of NaOH</td>
<td>· 0.072 mL added, white gel +0.5 mL, more precipitate</td>
<td>· 0.072 mL, dark green solution with diffuse light suspension</td>
<td>· 0.072 mL added, blue gel on contact does not dissolve when shaken</td>
<td>· 0.072 mL added, rust-colored gel on contact does not dissolve when shaken</td>
<td>· 0.072 mL added, dark green gel on contact does not dissolve when shaken</td>
<td>· 0.072 mL added, white precipitate formed +12.0 mL, clear*</td>
<td>· 0.5 mL added, white precipitate formed</td>
<td>· 0.25 mL, grey-pink color seen +7.0-8.0 mL, took 1.0 mL subsample +3.5 mL, clear*</td>
<td>· 0.072 mL added, dark blue color shift and slightly cloudy</td>
</tr>
<tr>
<td>Upon addition of NH₂CH₂COOH</td>
<td>· added, retained clear</td>
<td>· added, color shifted to indigo remaining clear</td>
<td>· added, no change</td>
<td>· added, dark brown-red color shift, remaining clear</td>
<td>· added, yellow color at least doubled in intensity</td>
<td>· added, remained clear</td>
<td>· added, solution appeared lighter (more dilute) green</td>
<td>· added, solution darkened to deep blue</td>
<td>· added, no change</td>
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Table 2: Testing Relative Effective Chelation in the Presence of Glycine

<table>
<thead>
<tr>
<th>(+Glycine)</th>
<th>Al(NO₃)₃</th>
<th>Cr(NO₃)₃</th>
<th>Co(NO₃)₂</th>
<th>FeCl₃</th>
<th>FeSO₄</th>
<th>Zn(NO₃)₂</th>
<th>Ni(NO₃)₂</th>
<th>Cu(NO₃)₂</th>
<th>MnCl₂</th>
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<tbody>
<tr>
<td>Upon addition of control volume of NaOH (0.072 mL)</td>
<td>White ppt.</td>
<td>Dark green solution with light precipitate</td>
<td>Blue gel precipitated and disappeared relatively slowly when stirred</td>
<td>Dark brown ppt, dissolved with vigorous stirring</td>
<td>Blue-green gel precipitate dissolved into a cloudy yellow solution</td>
<td>White pop disappeared as solution cleared</td>
<td>Shifted from green to blue color</td>
<td>Dark blue gel dissipated when mixed</td>
<td>Light yellow gel disappeared into solution slowly</td>
</tr>
<tr>
<td>Other Additions</td>
<td>none</td>
<td>none (remained cloudy)</td>
<td>+0.25 mL, blue pop disappeared</td>
<td>+0.5 mL, precipitate remains</td>
<td>none (remained cloudy)</td>
<td>+0.5 mL, no change recorded</td>
<td>+0.322 mL, color shifted to aqua-blue +0.25 mL, shifted to light blue +0.25 mL, cloudy</td>
<td>· 0.33 mL glycine added, cleared up into blue solution +0.33 mL NaOH, clouded</td>
<td>· 0.33 mL glycine added, solution cleared up</td>
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Conclusions:

1) Based on the results in the NaOH-added set in table 1, it appears that increased pH catalyzes or takes part in the formation of a complex with chromium ions in solution, turning green. It is confirmed in the text that chromium ions can complex with water under certain conditions (p 931). Aluminum and Zinc display amphoteric behavior under high or low pH conditions. Based on the concentration of ammonia (0.6M) and the Henderson-Hasselbalch equation, it becomes clear that their redissolution occurs below a pH of 11.54 [11.54 = 9.255 + log(0.6/0.0031)]. Zinc shifting to a grey-pink color may indicate a catalyzed complex formation, possibly with water, though no such color shift was seen with ammonia, that in reference texts is shown to complex zinc (pg. 932). 2) The results seen in Ni and Cu ion solutions are the most notable candidates for forming complexes with ammonia. These solutions showed color shifts or color stability even when diluted by the clear ammonia solution. Of these two, nickel seemed to be more adept at complexation directly with ammonia because no cloudiness was observed. Cr, Co, and both oxidation states of Fe gave gels or jelly-like precipitates of varying color. While this is not conclusive, it may be possible that complexed ions were forming on the solution interface between the clear solution and gel. This could indeed explain the gel-like property of such precipitates. If the above assumption is correct, another inference drawn from ongoing color changes within such precipitates clearly separated from the remaining original solution may indicate that slow reaction kinetics could eventually incorporate the added ammonia into such hypothetical complexes in these cases. Copper and Cobalt are also confirmed to complex with ammonia in the reference text (pg. 944 and 932, respectively). 3) Results from table two show that all ions seem to form chelated complexes with glycine except aluminum, the only non-transition metal tested. The most quickly-forming complexes “popped,” with no remaining cloudiness, indicating the fastest chemical kinetics. The order of reactivity from greatest to least based on this criterion is Ni, Zn, Cu, Co, and then Fe (III). Manganese remained untested beyond the control addition of NaOH. Other solutions that changed color remained slightly cloudy. Since this was in a beaker with a one-to-one ratio of glycine to the tested metal ion, the slow kinetics of complexation postulated above is confirmed—these solutions would likely clear up as the integer ratio of at least 1:1 glycine to metal ions should be expected to be reached. Finally, copper and zinc were tested with additional integer ratios of glycine and found to reform clear solutions of shifted color, showing that it should be possible to form such additional chelated complexes with other transition metal ions given the time for kinetics to allow for completion of such reactions. These chelated complexes seem to hold up to higher hydroxide concentrations without giving up their chelated metal ion, because the anion portion of glycine as a zwitterions, regardless of whether it is a ligand, allows for ionic interaction with the hydroxide ions, in essence keeping them bound and away from the metal that remains in solution as a result.