

Demonstrations as a Tool for Ironing-Out Misconceptions:

III. A Note on the Reaction $\text{Pb}^{2+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \rightarrow \text{PbI}_2(\text{s})$:

Exceptions from the *a priori* Expectations

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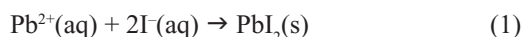
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Abstract

The precipitates formed upon the action of aqueous solution of potassium iodide on aqueous solutions of lead(II) nitrate and lead(II) acetate, respectively, are different. The assumption that in the presence of acetate a double salt $\text{Pb}(\text{CH}_3\text{COO})\text{I}$ has been formed, was ruled-out by IR spectroscopy. Some simple additional experiments prove that the precipitate, in the latter case, is actually due to lead(II) hydroxide iodide, in good agreement with the appearance of the IR spectra.

Introduction

In the general chemistry course, but also in analytical chemistry (when talking about characteristic reactions used in qualitative analysis of cations/anions [1,2]) one finds the following reaction:



and it is often mentioned as one of the reactions suitable for identification of the presence of lead in a given solution, for the precipitate is readily recognized by its bright yellow color. Also, there are several nice demonstrations that are based on the above reaction [3–5] (similar demonstrations could also be found on the World Wide Web too [6–8]). The most effective are those including cooling of hot and saturated water solution of lead(II) iodide [4]. The latter salt has a property of being sparingly soluble in cold water, but fairly soluble in hot water. On cooling of its saturated water solution, PbI_2 crystallizes in the form of small golden-yellow needles that are readily precipitated (due to the relatively high density of the salt, as well as due to the large size of the PbI_2 particles obtained in this way).

The important thing is that, the way eq. 1 is written (i.e. in ionic form), it is a source of a misconception. One may conclude that no matter what lead(II) salt is used, the addition of aqueous solution of potassium iodide (or, for that matter of any other soluble ionic iodide) will result in precipitation of yellow PbI_2 . This is not true, as will be demonstrated further. In what follows, we will describe a set of research procedures that enabled us to identify the nature of unknown precipitate.

The Problem

Knowing for many years the above chemical reaction, and working always with aqueous solutions of lead(II) nitrate, it happened once that we simply used stock solution of lead(II) acetate, for we thought we know it doesn't matter. A pale yellow precipitate was formed immediately. Although the color is similar to the bright yellow color of PbI_2 (cf. Fig. 1) the pale yellow precipitate was practically

insoluble both in cold as well as in hot water. It became obvious that the two precipitates are chemically different. One had to answer the question: what is the chemical nature of the pale yellow substance, and why are the precipitates obtained from nitrate and acetate different?

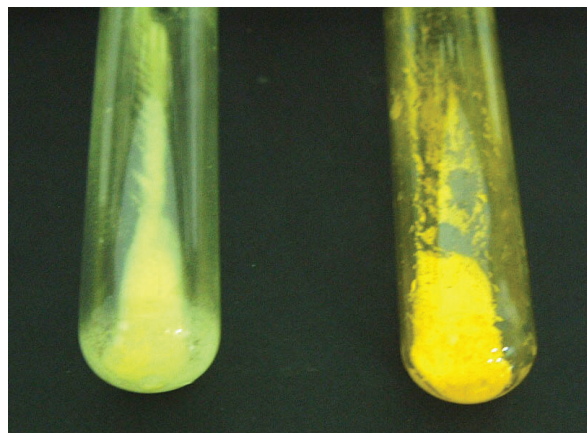


Figure 1
The precipitate obtained upon the action of $\text{KI}(\text{aq})$ on aqueous solution of lead(II) acetate (left) and lead(II) nitrate (right).

At first it seemed logical to assume that a double salt was formed, possibly $\text{Pb}(\text{CH}_3\text{COO})\text{I}$. However, this assumption had to be confirmed in some way. IR spectroscopy seemed to be both fast and convenient method for the above task.

IR Spectroscopic Measurements

The IR spectra of the pale yellow precipitate and of KCH_3COO were recorded on the Perkin Elmer System 2000 FT-IR interferometer. The substances (1–2 mg of each) were homogenized with 300 mg KBr and pressed on a hydraulic press, at a pressure of 1 GPa. The potassium acetate was recorded for purposes of comparison (if the two salts contain acetate anions, the spectra are expected to show some resemblance).

Experimental conditions. Both background and sample spectra were acquired with 8 scans, on an unpurged instrument. For more efficient elimination of problems

due to non-compensations of H₂O and CO₂ bands, a Perkin-Elmer Spectrum Software package [9] was used. A standard resolution of 4 cm⁻¹ was used. Other data regarding the choice of instrument parameters were: apodization strong; OPD velocity 0.2 cm/s; interferogram bidirectional, double sided.

For low-temperature FT-IR spectroscopy, a Graseby-Specac low-temperature cell was used. Spectra were again analyzed from KBr pellets, while liquid nitrogen was used as a coolant.

Perkin-Elmer Spectrum Software package [9] and Grams/386 software package [10] were used for spectra acquisition and manipulation respectively.

IR Spectroscopic Results:

Motivation for Further Checks

The spectra are presented in Figure 2.

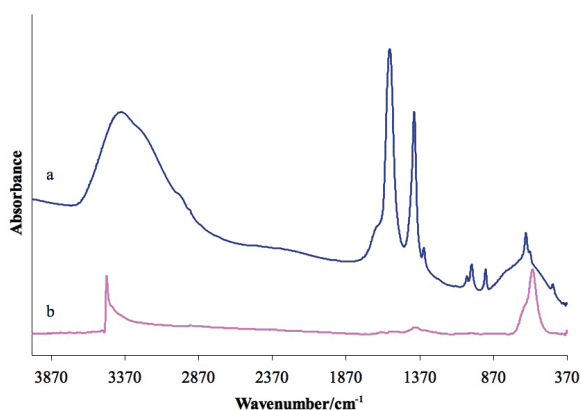


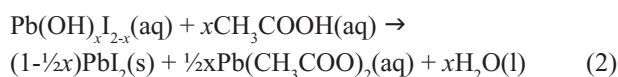
Figure 2 a, b FT IR spectra of potassium acetate (a) and the pale yellow precipitate (b). Note the distortion of the sharp band at ~ 3500 cm⁻¹, due to Christiansen effect.

Even an amateur in IR spectroscopy could safely conclude that the spectra are dramatically different. Obviously, the pale yellow substance contains no acetate groups. A more experienced spectroscopist will also note that, apart from appreciable quantities of “hygroscopic” water (water absorbed by the sample), the spectrum of the unknown does not seem to give evidence for a presence of any polyatomic anion. Two bands (at 3500 cm⁻¹ and at 604 cm⁻¹) strongly indicate a presence of OH⁻ anions. The sharp band at 3500 cm⁻¹ could easily be attributed to the O–H stretching vibration (the relatively high frequency and the band shape reveal that the OH⁻ anions are only weakly hydrogen bonded). The latter, rather broad band could be attributed to libration (a hindered rotation) of the OH⁻ anions. For a more detailed discussion of the IR spectra see Appendix 1.

What is the chemical nature of the pale yellow precipitate? The absence of other polyatomic anions but OH⁻, strongly suggests that the composition is Pb(OH)I, or at the very least, Pb(OH)_xI_{2-x}. If this is correct, then the differences between the nitrate and acetate salts could be explained in terms of the different pH values: water solution of lead(II) acetate is expected to have a higher pH value than the solution of the lead(II) nitrate (this is due to partial hydrolysis of both salts in solution, and the fact

that acetic acid is weak, while nitric acid is a strong one). PbI₂ is formed from the nitrate, as already known, but the conditions in the lead(II) acetate solution are more favorable for formation of the hydroxide salt. Let us also mention that the solubility of Pb(OH)₂ in water is much lower compared with that of PbI₂ [5], so at certain pH values the formation of the hydroxide salt instead of PbI₂ is fully justified.

If the above is correct, then one might reason that if the suspension of the pale yellow substance in water is acidified (say with CH₃COOH, to exclude the presence of other ions), then the Pb(OH)_xI_{2-x} could be converted to PbI₂, following the equation:



We then performed the above test: a water solution (c = 2 mol/L) of acetic acid was added to the pale yellow precipitate. The precipitate instantaneously turned bright yellow, in a complete accord with the expectations. It was then safely to conclude that the pale yellow precipitate is indeed Pb(OH)I, or Pb(OH)_xI_{2-x}. One more experiment (suggested by the referee), illustrates this notion even more vividly: small portions of diluted aqueous solution of KOH were added to a suspension of PbI₂ in water. The yellow color of the precipitate becomes paler and paler, till it is almost white (cf. Fig. 3). One could say that with each added portion, x increases from 0 tending to reach its maximum value of 1.

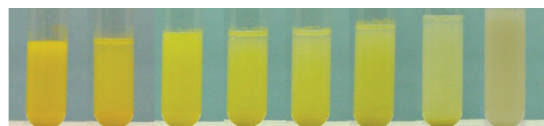


Figure 3 Changes in the color of aqueous suspension of PbI₂, upon addition of KOH(aq).

Conclusions

The experiment is of undisputable educational value. It teaches several things:

- chemically different substances can have similar (and sometimes almost identical) color;
- conclusions drawn by analogy (i.e. it is the same whether one should use a nitrate or an acetate salt) could be wrong;
- for many precipitates it is important to monitor the pH value of the medium, since hydroxide salts can often be obtained instead of normal salts (e.g. bismuth salts transform very often to hydroxide salts, if the medium is not properly acidified);
- once the research procedure has been performed as explained, it could be effectively modified into a serial (i.e. “a sequence of small experiments leading, step by step, to the desired goal” [11]), without using IR spectroscopy at all (this is important, as the use of IR instrument during lectures is highly impractical, if not impossible).

One should note that in a research experiment (procedure), it is not necessary that the result is indeed new and original.

The point of it is that the result is a novelty for the class or for the class and the instructor. A working assumption is formulated: in our experiment we assumed that the pale yellow precipitate is a double salt lead(II) iodide-acetate. Then, a strategy has to be developed (like using IR spectroscopy) to confirm the assumption. In our case the assumption failed, as no presence of acetate ions could be detected. Further, in order to reveal the unknown (the chemical nature of the pale yellow precipitate), another logical assumption might be necessary (the spectra suggested it is a hydroxide salt and an independent proof of this was offered by a simple chemical reaction of the pale yellow precipitate with acetic acid, performed in a test tube).

Safety Tips and Disposal

Safety goggles and gloves should be worn at all times during the demonstration.

All water soluble lead salts are very poisonous! The waste must be disposed according to local safety regulations. It might be useful to know that PbS is practically insoluble precipitate, so the waste could first be converted into PbS and then disposed (e.g. flushed under the drain).

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Appendix 1

To further confirm the assignment, we decided to run some spectra at the temperature of liquid nitrogen (LNT). Experience shows (there are sound theoretical reasons too) that on cooling the vibrational bands due to the bending O–H vibrations get sharper (the same applies to the OH stretchings, but the effect is less pronounced). Frequency shifts are also often evident: for medium and strong hydrogen bonds, on cooling the OH stretchings exhibit red shift and the bending (librational) bands exhibit blue shifts. If the hydrogen bonds are both weak and highly bent, the stretching OH band might show a blue shift, the latter being also characteristic for bifurcated hydrogen bonds [12]. The room temperature (RT) and liquid-nitrogen temperature (LNT) spectra are given in Fig. 4.

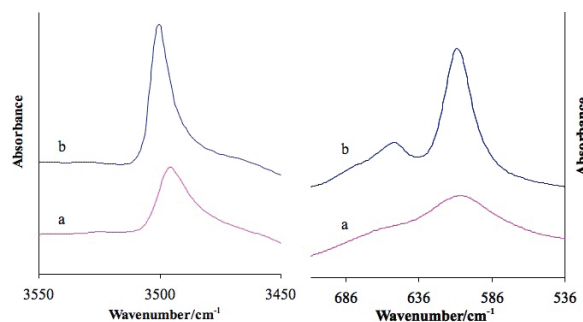


Figure 4 The OH stretching (left) and bending (right) regions of the FT IR spectra at room (a) and liquid nitrogen (b) temperature of the pale yellow precipitate.

It is evident that both intense bands are much sharper at LNT. There is a minor blue shift on cooling (5 cm^{-1}) of the OH stretching band. These findings confirm that the only type of polyatomic anions present are OH^- anions (these participate not only in formation of weak, but also of rather bent hydrogen bonds, as evidenced by the blue temperature shift of the OH stretching band).

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