INQUIRY-BASED EXPERIMENT ON THE SYNTHESIS OF $K_3[Fe(C_2O_4)_3].3H_2O$

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Abstract. In the present paper inquiry-based learning strategy applied to the laboratory work (inquiry-based labs) was used to synthesize and characterize the potassium ferrioxalate complex. The implemented educational strategy showed to be an excellent methodology to develop experimental activities of inorganic chemistry. In this work the synthesized compound was identified and characterized by infrared spectroscopy, X-ray diffraction, magnetic susceptibility and photosensitivity under UV/Vis irradiation. The experimental procedures were explored and implemented by the students, under orientation and inspection of the teacher. The students showed their abilities to formulate „scientific questions“ and hypotheses, search scientific literature and write and discuss scientific results, which constitutes an excellent exercise about the experimental science construction.

Keywords: chemical education, inquiry-based experiment, synthesis of inorganic compounds, potassium ferrioxalate

Introduction

One of the goals of teaching science should be teaching the process of science; but unfortunately the typical lab-manuals include experiments that provide detailed procedures, directions regarding what data to obtain and when to take particular measurements, organized data tables, and the step by step calculations or analysis required reaching a conclusion [1]. However, this teaching approach does not lead the student to learn the typical science procedure to solve problems, and on the contrary it can accustom the learner to receive mechanical instruction without generating of thinking skills.

The aim of education in general and higher education in particular, is to produce independent, responsible and capable people [2]. For that reason, during the past fifteen years, a significant movement to reform science education has occurred in response to the growing need for a scientifically literate citizenry who are prepared for a technologically advanced and globally competitive democratic society [3,4]. In this sense, several science education approaches have been proposed [5-8], in which the development of a critical thinking with abilities to search scientific literature, to interpret technical information and to generate explanations and hypotheses about the scientific phenomena, concepts or procedures is the major aim of the teaching process. In these educational approaches one can highlight the Inquiry-Based Instruction Strategy [9,10], which is a teaching methodology founded in the *constructivism*, it involves *problem solving* approach and is strongly related with the real methodology of science [5,11]. Recently, several papers have claimed to use the inquiry-learning methodology for lab works (inquiry-based labs), indicating the features, advantages, opinions and conceptions of students and teachers [9,10,12,13]. Here, questions and hypotheses raised in the course of the activities represent a good exercise of scientific attitude; these permit to relate the theoretical concepts with some practical applications and help to transfer the school knowledge to everyday contexts [8].

The inclusion of the inquiry-based instructional methods in the chemistry classroom has been widely advocated in the past decade from a variety of sources in the U.S.A, including National Standards and editorials and commentaries from the Journal of Chemical Education [10]. However, to our knowledge, the implementation of this methodology in Colombia has been very difficult as in the secondary school as in the higher education, and only a few teachers have shown to use this strategy. Perhaps the scarce use of the inquiry-based instructional methods in our country obeys to the higher requirement in time, effort, pedagogical knowledge and resources, than the traditional laboratory methodology (cookbook-style lab manuals).

On the other hand, syntheses of coordination complexes are particularly attractive because they are easy to carry out in high yield, they involve relatively simple stoichiometries, and they provide a variety of highly coloured compounds [14]. In this context, potassium trioxalatoferrate(III) trihydrate $\mathbf{(K_3[Fe(C_2O_4)_3].3H_2O)}$, also called as potassium ferrioxalate, is a green crystalline-compound of octahedral geometry, coordinated with three bi-dentate oxalate ($C_2O_4^{=}$) ligands [15]. This compound is a very interesting photosensitive material, and therefore it is commonly used as actinometer to determine monochromatic radiant fluxes from the ultraviolet to visible wavelengths [16, 17]. In this sense, this work presents the synthesis of ferrioxalate by means of the inquiry-based experimental methodology, with the object of illustrating this science educational strategy in inorganic chemistry. The main goal of this paper is the pedagogical discussion, but additionally although the synthesis of this compound has been reported in several papers [18-22], physical and chemical results discussed here are originals (collected from our experiments) and they have not been reported in other article.

Methodology

The experimental work should be initiated with a short introduction of the teacher about the importance of potassium ferrioxalate (among several synthesis topics for other possible works) in order to motivate the students. Then he may raise the following questions: (1) Which are the main chemical features of potassium ferrioxalate? (2) How can I synthesize the potassium ferrioxalate? (3) How can I recognize the potassium ferrioxalate? (4) What hazards could the synthesis of this compound have? (5) How could I assess the photosensitivity of potassium ferrioxalate? (6) Why is this compound green?

Next, the students should place each question on the appropriate circle of the Fig. 1, and then to initiate the literature search to make a small project about the synthesis of potassium ferrioxalate. They must develop and extend the initial questions; for example, in the question number 2: What is the best procedure? What stoichiometric relationship should be used? What materials are needed? What physicochemical parameters should be controlled?

Teacher acting as referee must review and discuss/correct the written project for each student before executing of the work. In this point it is necessary to put large attention to the writing style of the student because of they should acquire abilities to write in scientific form. Many authors in chemical education claim about the great importance of writing in chemistry, emphasizing that an effective written communication is a fundamental aspect to develop in the chemistry curricula [23,24].

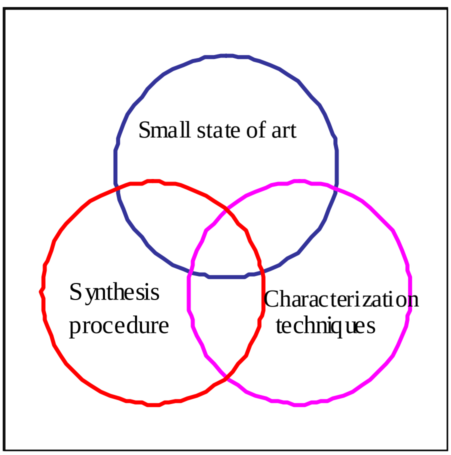

Fig. 1. Scheme of organization of the small project based on the inquiries mentioned above

In the present experimental section we are showing the synthesis procedure and characterization reporting for one group (two students) of work in a laboratory course of inorganic chemistry in the National University of Colombia.

Synthesis procedure

In a typical procedure, the students prepared potassium ferrioxalate by mixing potassium oxalate and ferric chloride solutions from analytical grade reagents (Merk) and distilled water. Consequently, a stoichiometric quantity of a 2.0 M solution of $FeCl_3$ was slowly added to a beaker containing a 3.0 M solution of $K_2C_2O_4$ in constant stirring at room temperature. The final mixture was cooled at 0 ^oC to allow the crystallization of compound. After crystallization the green solid was separated by filtration and twice recrystallized in distilled/deionized water. Finally the solid was dried in a desiccator.

Sample characterization:

About the question 3, the students reported the characterization by infrared spectroscopy using a Perkin Elmer (FT-IR) Paragon 500 equipment, diluting the sample in KBr (2 mg of sample in 200 mg of KBr). Additionally they analysed the potassium ferrioxalate by X-ray diffraction (Philips PW 1820, with Ka-radiation: 1.54056 Å) and magnetic susceptibility (Johnson Matthey magnetic susceptibility balance). Finally photosensitivity of the synthesized compound was tested by a commercial 4 watts UV/VIS lamp installed by the teacher.

Results and discussion

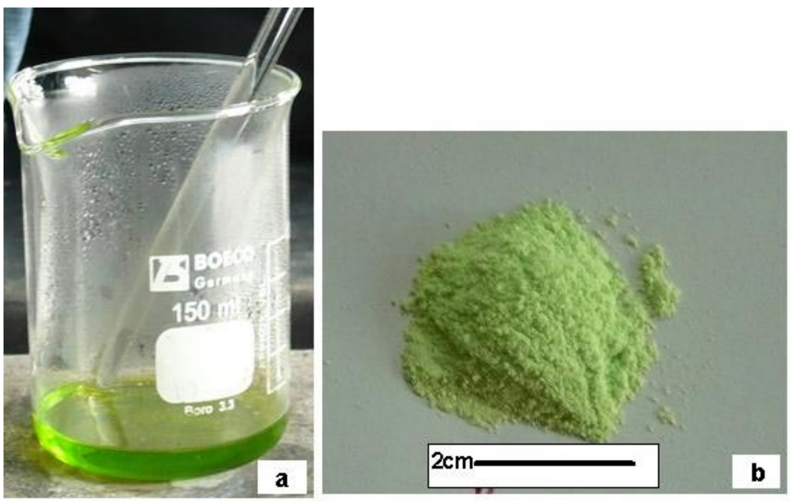

Fig. 2. Prepared potassium ferrioxalate: a) in solution, b) crystallized and dried

Fig. 2 shows the images of the obtained compound (green). IR spectrum (Fig. 3) was analysed and discussed between the students and the teacher, finding that all bands observed in the spectrum correspond to the ferrioxalate compound structure (1714, 1680, 1391, 1273, 1255, 891, 804, 531, 500 cm-1) and hydration or adsorbed water (3429 cm-1) [25].

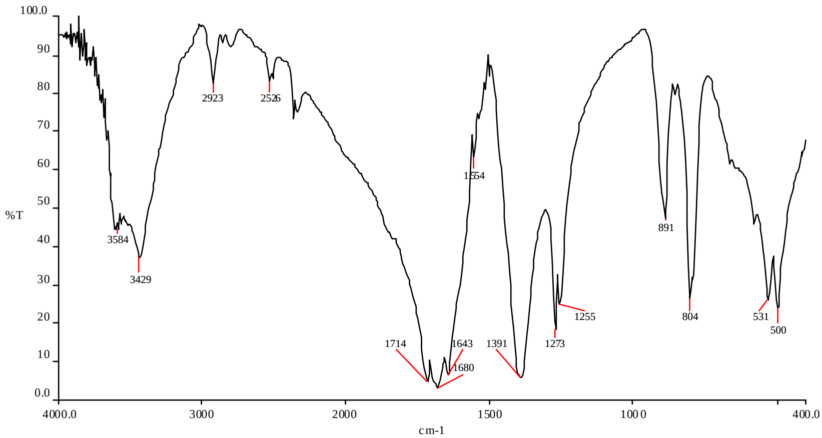

Fig. 3. IR spectrum of the synthesized potassium ferrioxalate

According to the methodology proposed here the author does not wish to describe the interpretation of IR spectrum, but he can suggest some important questions to orientate the discussion of teachers and students that may choose this paper as a classroom or lab material. The following questions should be raised: (1) How is the coordination structure of the ferrioxalate ($[Fe(C_2O_4)_3]^{3-}$) ion? (2) Which are the IR signals corresponding to the oxalate ion? (3) Which are the IR signals corresponding to the Fe-O bond? (4) Which are the IR bands of water? (5) For each case, what signal corresponds to stretching and which to bending?

On the other hand, X-ray diffraction results (Fig. 4) were discussed with the teacher, and the different 2-theta position were compared with the literature data. The Miller indices (hkl) were assigned from the paper of Dakhel [15]. Additionally, the interplanar distances (*d*) were calculated by an interpretation exercise from Bragg's equation: $n\lambda = 2dsen\theta$; where λ is the wavelength of diffractometer (1.54056 Å), θ is the diffraction angle and n = 1 (Table 1).

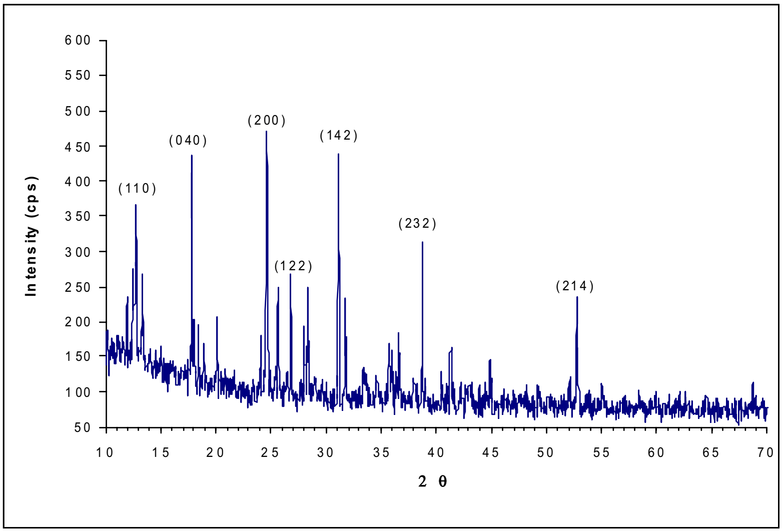

Fig. 4. Powder X-ray diffraction pattern of the synthesized compound: potassium ferrioxalate

Table 1. Positions of the most important peaks on the diffractogram of Fig. 4

2 theta	θ	Sin θ	d	(hkl)
12.76	6.4	0.111	6.93	(110)
13.35	6.7	0.116	6.63	-
17.76	8.9	0.154	4.99	(040)
24.64	12.3	0.213	3.61	(200)
25.68	12.8	0.222	3.47	-
26.85	13.4	0.232	3.32	(122)
28.36	14.2	0.245	3.14	-
31.11	15.6	0.268	2.87	(142)
31.71	15.9	0.273	2.82	-
38.65	19.3	0.331	2.33	(232)
52.72	26.4	0.444	1.73	(214)

About the X-ray diffraction analysis one may formulates the following questions to guide the discussion: (1) What is a crystalline solid? (2) How does X-ray diffraction occur? (3) What does Bragg's equation describe? (4) What are the Miller indices? (5)

How can I determine the Miller indices? (6) What is the potassium ferrioxalate crystal system? (7) How can I determine the cell parameter of a crystal?

Table 2. Magnetic susceptibility of synthesized compound (potassium ferrioxalate) assuming three hydration water molecules

***X*g**	***X*m** = Xg x Mw	μ (BM)
3.14x10^{-05}	15.431x10^{-3}	6.02
3.10 x10^{-05}	15.245 x10^{-3}	5.98
2.93 x10^{-05}	14.374 x10^{-3}	5.81
3.17 x10^{-05}	15.556 x10^{-3}	6.04
Average of μ = 5.96		

μ = magnetic moment [Bohr magnetons: BM], X_g = magnetic susceptibility per gram, X_m = molar magnetic susceptibility [(MB)^2/K], M_w = molecular weight.

The magnetic susceptibility results are showed in the Table 2. The magnetic moment (μ) was determined using the equation $\mu = 2.84\sqrt{(X_m T)}$, where X_m is the molar magnetic susceptibility and T is the absolute temperature. The values of μ were determined four times, and the average value of 5.96 BM (Bohr magneton units) may be compared with the magnetic moment of spin (μ_s) ca;culated for five unpaired electrons. $\mu_s = \sqrt{n(n+2)}$, where n is the unpaired electron number. For five electrons (Fe^{3+} has d^5 configuration) the calculated μ_s is 5.92 BM. This result indicates that the Fe^{3+} in the synthesized ferrioxalate complex has a high spin configuration (weak field condition in the crystal field theory).

About this section the teacher could orientate the discussion as follows: (1) what is the electronic configuration of Fe^{3+} as in weak field as in strong field conditions; (2) how many unpaired electrons there are in each of the configurations described above; (3) calculate the spin magnetic moment for iron in each of the configurations described above; (4) from the experimental data (magnetic susceptibility results) which electronic configuration can be assigned to the Fe^{3+} in the potassium ferrioxalate complex; (5) which is the position of oxalate ion in the spectrochemical series; (6) how do you explain (from crystal field theory) the colour (green) of the potassium ferrioxalate complex; (7) how do you explain the deviation of magnetic moment experimentally determined, with respect to the spin magnetic moment determined with the equation $\mu_s = \sqrt{n(n+2)}$; (8) calculate the crystal field stabilization energy (CFSE) (in Δ_0 units) for the Fe^{3+} ion in the potassium ferrioxalate complex.

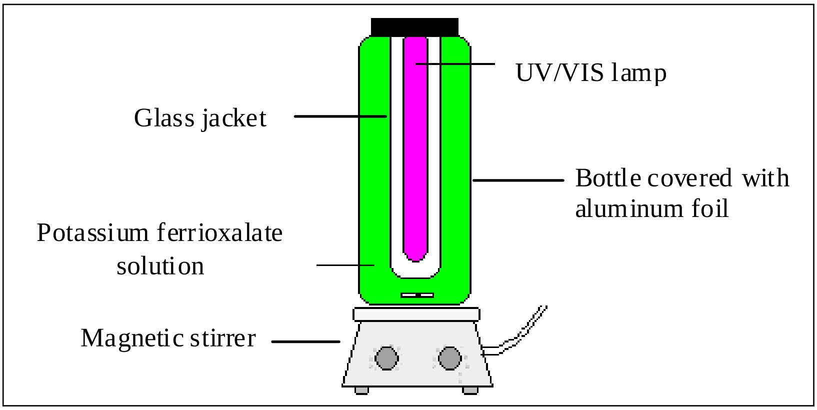

Fig. 5. Experimental set up to determine the photosensitivity of potassium ferrioxalate

Finally, the photosensitivity of potassium ferrioxalate was observed by exposing of a solution volume of this compound (in distilled/deionized water) to the irradiation of an UV/VIS lamp (Fig. 5), to produce ferrous ions and its subsequent detection by means of the formation of $[Fe(1,10\text{-phenantroline})_3]^{2+}$ complex. After that, the absorbance of complex was measured at 510 nm wavelength using a UV/VIS spectrometer. This experiment corresponds to a typical *actinometry procedure* described in the literature [16,17].

Table 3. Absorbance values of samples irradiated at different times, and containing $[Fe(1,10\text{-phenantroline})_3]^{2+}$ complex. For each absorbance value, the blank (value for the solution before irradiation) was subtracted and therefore at zero time the absorbance was zero

Time (min)	Absorbance
0	0
5	0.471
10	0.605
20	0.710
25	0.728
30	0.813

Table 3 shows the increase of absorbance values when the time is increased, indicating the formation of more quantity of $[Fe(1,10\text{-phenantroline})_3]^{2+}$ complex as a result of the production of ferrous ions under irradiation. Therefore these results verify the initial photoredox reaction of potassium ferrioxalate as a complementary characterization.

In this section, the teacher may direct the discussion as follows: (1) what photoredox reactions can potassium ferrioxalate undergo; (2) why is potassium ferrioxalate photosensitive; (3) what is the structure of ferrous-1,10-phenantroline complex; (4) how do you imagine the experimental set up to assess the photosensitivity of potassium ferrioxalate?

Conclusion

Inquiry-based learning strategy applied to the laboratory work (inquiry-based labs) constitutes an excellent methodology to develop experimental courses of science, such as the synthesis and characterization of compounds in inorganic chemistry. In this sense, the employed methodology led to the appropriate preparation and complete identification of potassium ferrioxalate complex ($K_3[Fe(C_2O_4)_3].3H_2O$) by means of procedures explored and implemented by the students, under orientation and inspection of the teacher. Additionally, with this educational strategy the students could have the experience to formulate „scientific questions“ and hypotheses, looking for scientific literature and writing a small project to work at the lab. Finally, the procedures, the results and the questions exposed in the present paper constitute a good exercise to discuss in the classroom activities of theoretical inorganic chemistry courses.

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