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Why Is There Cyanide in my Table Salt? Structural Chemistry of the Anticaking Effect of Yellow Prussiate of Soda ($\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$)

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S Supporting Information

ABSTRACT: Yellow Prussiate of Soda (YPS, $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$) is an approved anticaking agent in table salt. Given that it is a cyanide salt, its use as a food additive is surprising. Recent findings on the mode of action of submonoatomic layers of YPS on NaCl crystals to act as an anticaking agent through nucleation inhibition are presented and its low toxicity is rationalized. The molecular mechanics of the anticaking action are relatively easy to understand for students in general chemistry or sophomore inorganic courses as they involve the archetypal cubic sodium chloride crystal structure and simple steric and electrostatic arguments. The molecular-level explanation reinforces the notion of how structure and charge affect the properties of matter and may also serve as entry toward a classroom dialogue of how ionic lattices are formed. A simple naked eye analytical method of detecting YPS on store-bought table salt in the form of the pigment Prussian Blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$) can be utilized as a related demonstration, to visualize the presence of YPS in table salt, or a quick laboratory exercise for inorganic chemistry.

KEYWORDS: First-Year Undergraduate/General, Inorganic Chemistry, Analogies/Transfer, Consumer Chemistry, Crystals/Crystallography, Solids



INTRODUCTION

Table salt (NaCl) improves the flavor of our food and provides the essential nutrients sodium and chloride. Cheap and ubiquitous today, salt was once a highly valuable commodity, making it an intriguing subject of discussion.¹ The cubic sodium chloride structure of alternating Na^+ and Cl^- ions is commonly introduced in General Chemistry classes as the archetypal example of an ionic lattice structure.

Table salt is hygroscopic, i.e., it absorbs water from the air, particularly in humid environments and when it contains traces of other hygroscopic salts, such as MgCl_2 .² The outer layers of the salt crystals dissolve, making them susceptible to agglomeration when the moist layers dry up again. This causes problems in the salt industry that handles enormous quantities of salt. For instance, the mountains of granular rock salt that are being stocked to de-ice roads and sidewalks could fuse into giant unusable blocks of salt. On a smaller scale, we enjoy free-flowing salt in our salt shaker on the dining table. To prevent the caking of salt, anticaking agents are added.

This *Journal* overviewed common additives in salt, among them anticaking agents.² Frequently used anticaking agents are calcium silicate (CaSiO_3), tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), silicon dioxide (SiO_2), sodium aluminosilicates (e.g., the zeolite $\text{Na}_2\text{Al}_2\text{Si}_{14}\text{O}_{32} \cdot 3\text{H}_2\text{O}$), sodium bicarbonate (NaHCO_3), or rice flour. Perhaps much less known is that a cyanide salt, Yellow Prussiate of Soda (YPS, $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$),³ may also be present as an anticaking agent in table salt formulations (Figure 1).²

Given the high toxicity of cyanide, the use of YPS as an approved food additive is puzzling at first. However, the cyanide within YPS is bound very tightly (the formation



Figure 1. Partial label of table salt, purchased at a local supermarket, listing Yellow Prussiate of Soda as an ingredient.

constant, K_b of $[\text{Fe}(\text{CN})_6]^{4-}$ is 10^{36}),⁴ resulting in the low toxicity of YPS. The quantities of YPS consumed with table salt are also minute (for further information on the toxicity of YPS, see the Supporting Information).

It may be safe, but how does it act as an anticaking agent? The addition of baking soda, silicon dioxide, or rice flour as an anticaking agent is intuitively understood: After all, the concept of coating sticky surfaces with substantial amounts of an inert powder to render them nonsticky is a familiar concept (flour on dough, talcum powder on medical examination gloves, etc.). Aluminosilicates act as molecular sieves, binding water, making their mode of action also readily clear. However, to understand how the addition of a very small quantity of a cyanide complex

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of iron can prevent the caking of salt requires a look at the atomic-level mechanism of the anticaking action.

The influence of YPS on the crystallization of NaCl was studied 50 years ago,^{5a} but the fundamental chemical interaction between the ferrocyanide ion and the sodium chloride crystal surface remained speculative until reports in 2012 by Bode et al.⁵ His group used two advanced methods to probe the surface features: Surface X-ray diffraction (SXRD),^{5a} and *in situ* atomic force microscopy (AFM).^{5b} These techniques provided direct experimental proof for a detailed explanation of the mechanism of YPS anticaking activity, soundly dispelling an earlier notion that YPS also functioned by the absorption of water.² The atomic-scale understanding that emerged from these investigations will be summarized below. In addition, we present a simple and rapid naked eye test to detect YPS in table salt by addition of Fe^{3+} to table salt on a spotting plate, suitable as a demonstration or laboratory experiment.

FINDINGS

Anticaking agents may also function by inhibiting crystal nucleation or by modifying the external shape of a group of crystals (termed the crystal habit). YPS functions through both effects. Salt grown from brines containing YPS forms dendritic (star-shaped, with many branches) crystals.⁶ Even when the cubic crystals are coated with YPS, dendritic growth is observed on their surface.^{5b} Dendrite salt has a lesser propensity to cake together than the smooth-faced cubic crystals of unmodified table salt. Table salt crystal growth rates are also inhibited by YPS. The mechanisms behind both effects were studied by Bode and co-workers.⁵

This research group grew defect-free NaCl crystals ($3 \times 3 \times 3 \text{ mm}^3$) and deposited submonoatomic layers of YPS on their surfaces by evaporation of dilute methanolic YPS solutions. Surface X-ray diffraction (SXRD) was then used to investigate the structure of the crystal surfaces.^{5a} SXRD uses high-intensity monochromatic X-ray radiation to measure signals arising from diffuse diffraction by the atoms on the crystal surface and upper sorption layers. This technique therefore provides insight into the surface structure. An unmodified NaCl crystal served as a blank.

The technique allowed the observation of layers of adsorbed water on the pristine, YPS-free crystal surface (Figure 2A). Changes in relative humidity resulted in the formation of increasingly disordered layers of adsorbed water, from one to four molecules thick. The oxygens in the first layer of water are found to be located, as expected, directly above the Na^+ ions.

Data acquired for the YPS-modified surfaces suggested the following model:^{5a} Because of a good shape and size match (<1% size difference), octahedral pentaanionic $[\text{NaCl}_6]^{5-}$ units on the surface of the crystal are readily replaced by octahedral tetraanionic $[\text{Fe}(\text{CN})_6]^{4-}$ complexes. The ferrocyanide ions are positioned with the iron atom at the sodium ion location (Figure 2B). Four cyanide ligands are pointing toward the four neighboring sodium cations on the surface, one cyanide ligand sticks down, replacing a chloride ion in the bulk crystal, and the final cyanide ligand sticks out into the water layers.

In the pristine NaCl crystal, a linear sequence of $\cdots\text{Na}-\text{Cl}-\text{Na}-\text{Cl}\cdots$ with metal-bridging anions occurs (Figure 2A), but the equivalent sequence between cyanide anions and iron cations cannot take place because the cyanides cannot bridge two iron cations. Instead, the sequence $\cdots\text{Na}-\text{NC}-\text{Fe}-\text{CN}-\text{Na}\cdots$ repeats across the surface of the crystal (Figure 2C). Thus, at most one in four Na^+ at the surface may be replaced with Fe^{2+}

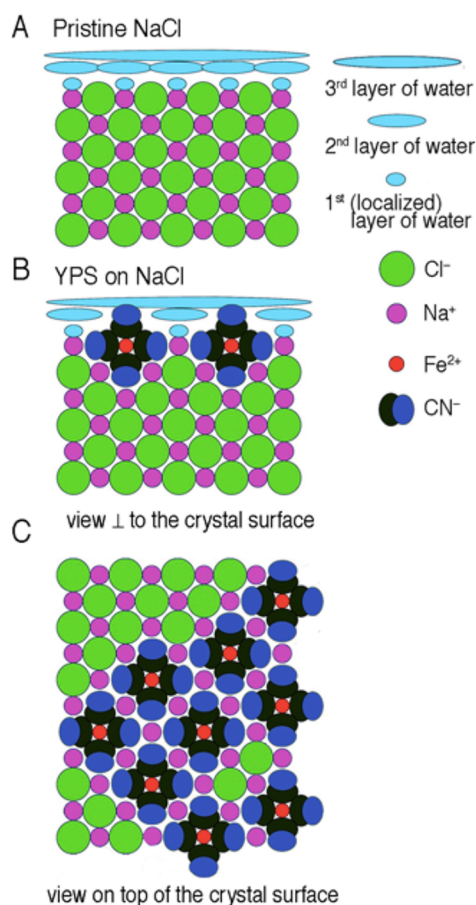


Figure 2. Models of the interaction of YPS on the NaCl surface as determined by Bode et al.:^{5a} (A) Side view of the blank NaCl crystal with three adsorbed water layers on the NaCl surface; (B) location of the $[\text{Fe}(\text{CN})_6]^{4-}$ ions sorbed onto the NaCl surface; (C) top view of the NaCl surface showing areas with no YPS, areas of densest possible $[\text{Fe}(\text{CN})_6]^{4-}$ ion coverage, and areas of a less dense coverage. Figure adapted from ref 5a. Copyright 2012 American Chemical Society.

(1 in five Na^+ on pure geometric grounds plus one because of the higher charge of the Fe^{2+} versus Na^+). An even less dense coverage ($52 \pm 12\%$) is observed experimentally, without the buildup of crystalline multilayered or long-range in-plane ordered structures.

DISCUSSION

The charge of one ferrocyanide ion ($[\text{Fe}(\text{CN})_6]^{4-}$) is 4−, while that of the similarly sized and shaped hexachlorosodium ion complex ($[\text{NaCl}_6]^{5-}$) is 5−. This charge mismatch is the origin of the anticaking activity of YPS. To keep the total surface uncharged upon replacing one $[\text{NaCl}_6]^{5-}$ unit by one $[\text{Fe}(\text{CN})_6]^{4-}$ unit, one less sodium counteranion is needed. If $\text{Na}_4[\text{Fe}(\text{CN})_6]$ were to be incorporated into the bulk of the crystal by growth of a NaCl crystal on top of it (by, for instance, crystallization from brine formed from atmospheric moisture and a neighboring NaCl crystal), a sodium vacancy is needed to keep the crystal electrically neutral. This, however, is energetically (electrostatically) very unfavorable because this vacancy leads to an increased electrostatic anion–anion repulsion. Since the ferrocyanide ion cannot be incorporated into a bulk sodium chloride crystal and its tight binding to the surface does not easily allow desorption, crystal growth and the expression of interparticle bridges is inhibited, and the caking of sodium

chloride is effectively prevented. Other anticaking agents are charge-matched but provide steric inhibition to crystal growth.^{5a}

Bode et al. further explored the NaCl surfaces using *in situ* atomic force microscopy (AFM), a technique which utilizes a microscopic cantilever with a tip only a few atoms thick to scan the molecular-level topography of a surface. This provided images of the growths of single NaCl layers on NaCl crystal surfaces, allowing them to probe if, and to what degree, YPS slowed NaCl crystal growth. And indeed, the YPS coverage slowed or prevented crystal growth, with NaCl crystal growth observed to take place only off the small and irregularly spaced unaltered NaCl surfaces, leading to thin dendritic crystal forms.^{5b} Thus, with the help of sophisticated measurement techniques, a persuasive atomic-level explanation for the anticaking activity of YPS on NaCl crystals was provided.

■ DETECTION OF YPS IN SALT: A NAKED EYE COLORIMETRIC ASSAY

Ferrocyanide is a component of Prussian Blue, a family of generally insoluble complex dyes containing the mixed-valent iron hexacyano complex $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6]^-$ (additional information on the formation of Prussian Blue is provided in the Supporting Information). Their intense deep blue color and chemical stability have made them popular as textile dyes and in the visual arts. Reports in this *Journal* described the history, structure, and artistic uses of Prussian Blue.^{7–9}

Prussian Blue is commonly formed by addition of Fe^{3+} to ferrocyanide, but other methods exist which also result in its formation (see Supporting Information). The facile formation of Prussian Blue has been used as an analytical test for the presence of iron(II) or iron(III), cyanide, ferro-, or ferricyanides.¹⁰ The insolubility of Prussian Blue, combined with its deep blue color, results in low detection limits for these species ($0.25\ \mu\text{g}$ of $[\text{Fe}(\text{CN})_6]^{4-}$ can be readily detected in the experiment described below).¹⁰ The test is also largely insensitive to the ratio of the Fe^{2+} and Fe^{3+} species or the presence of a large excess of other ions (here, Cl^- and Na^+).

Thus, addition of a slightly yellow aqueous solution of FeCl_3 ($\sim 9\ \text{mM}$) to dry table salt that does not list YPS as an ingredient on a white porcelain spotting plate merely exhibits the color of the added iron(III) salt (Figure 3). In contrast, upon addition of the iron(III) solution to a table salt containing YPS, a blue-green color on the crystal immediately emerges. This is the color of Prussian Blue mixed with the yellow of the iron solution. A variation of this test can also be performed in brine solutions in test tubes, also allowing a UV–vis spectroscopic characterization of colloidal Prussian Blue (see Supporting Information).

■ CONCLUSIONS

Our general familiarity with table salt makes NaCl an excellent teaching tool, particularly when highlighting some surprising facts about this seemingly mundane household item. The discussion about the anticaking effects of YPS is suitable for students that are familiar with the general nature of crystals, the crystal structure of NaCl, electrostatic arguments (perhaps even crystal lattice energies), and the basics of coordination chemistry (complex anions), i.e. students in the second semester of general chemistry or in sophomore inorganic chemistry classes. The understanding of the atomic-level explanation for the anticaking activity of YPS brings home

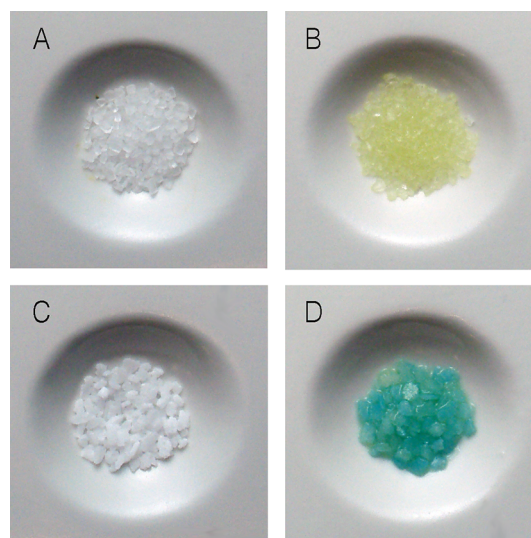


Figure 3. Store-bought table salt samples placed into the wells of a porcelain spotting plate with and without YPS, and before and after addition of $\sim 9\ \text{mM}$ aqueous solution of FeCl_3 . (A) Morton Natural Sea Salt with no additives. (B) Morton Natural Sea Salt + FeCl_3 ; the yellow tint is the color of the solution of Fe^{3+} . (C) Morton Coarse Kosher Salt containing YPS. (D) Morton Coarse Kosher Salt + FeCl_3 ; the bluish-green color indicates the presence of YPS by formation of Prussian Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$.

the key chemical concept that chemical structure determines the chemical and physical properties of matter.

We presented the discussion material to an inorganic chemistry class where it elicited a lively discussion about the mechanisms of crystal growth. The students were much surprised about the presence of YPS in many table salts; that fact piqued their interest.

The naked eye analytical method of detecting YPS as Prussian Blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$) is pedagogically flexible and can be utilized to demonstrate the presence of YPS in table salt or as a quick exercise for an inorganic chemistry laboratory, opening up a discussion of the role of YPS or structural aspects of Prussian Blue, particularly how Prussian Blue adopts a NaCl-like crystal structure. This *Journal* provides further material on Prussian Blue.^{7–9} The experiment also highlights how minute amounts of YPS (or cyanide or iron) can be readily detected using a classic wet chemistry assay.

■ HAZARDS

Use caution when handling the strong and very hygroscopic Lewis acid FeCl_3 and its acidic solutions (use safety glasses and gloves).

■ ASSOCIATED CONTENT

Supporting Information

Experimental description for YPS detection on a spotting plate or in solution, as well as additional information on the formation of Prussian Blue. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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