Chromium Reduced Schiff Base

Homemade fruit peel cleaner

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** Note: This report has two sections. The first section is titled " a) Chromium complexes" and the second section is titled "b) Homemade detergents". This is due to the fact that two separate projects were carried out in light of the COVID-19 pandemic.*

a) Chromium complexes

Abstract

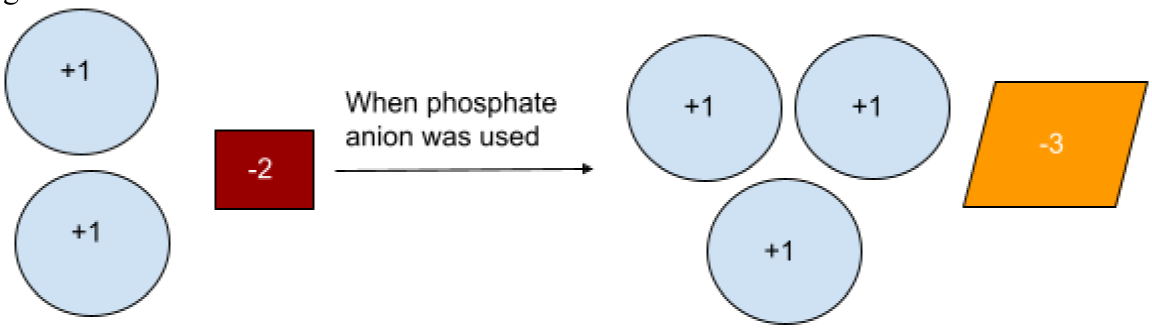
Transition metal coordination complexes can exist in a wide range of colors, and visible properties of coordination complexes are of chemical significance as they allow for the determination of chemical properties and structure of the compound. One particular complex of interest consists of a chromium metal ion coordinated with two reduced Schiff base (RSB) ligands and sulfate as the anion, which is a wine red color complex. In the project, the anion was substituted with phosphate with RSB derived from different amino acids. The color of the compound unexpectedly changed from wine red to purple and hence was analyzed with UV-vis spectroscopy to confirm the color change.

1. Introduction

Background information

Transition metal complexes are widely used in pharmaceuticals and as industrial catalysts due to their wide range of properties such as the ability to speed up reactions that involve the exchange of electrons between chemical compounds, and are able to interact with biological molecules [1]. An example is cisplatin, a platinum complex which is used to treat head and neck cancer [2]. For a charged transition metal complex, an anion is required to balance the charge to ensure the whole compound is stable and contains a net zero charge [3]. It is established that changing the anion of the metal complex will cause the change of properties of the complex and can even affect the stability of the complex [4]. In the project, the anion of a positively-charged transition metal complex with the changed and the properties of the compound as a result of the change in compound will be investigated (Figure 1, below).

Figure 1:



Legend:

Red-brown - Anion

Blue circle - one unit of Chromium complex

Rectangle - Sulfate anion with -2 charge

Parallelogram - Phosphate anion with -3 charge

Note: The diagram is not drawn to scale

<u>Problem faced</u>

The synthesis of the chromium RSB complex with phosphate anion was proposed as phosphate is present in many biological molecules including DNA [5], hence may allow the synthesized complex to possess biological activities. Phosphates are also readily accessible in the laboratory.

2. Solution Design

Throughout the project, the anion of the complex was changed from sulfate to phosphate. The synthesis of the Chromium RSB complexes will be repeated with varied amino acids to ensure that any change in the properties of the resulting compound is consistent with the experiment results.

3. Methods

An amino acid[1] and 2-pyridinecarboxaldehyde was reacted in a 1:1 molar ratio in a solution, with excess potassium hydroxide as a catalyst, to form a Schiff base. Thereafter, the Schiff base was reduced by addition of excess sodium borohydride in an iced water bath, forming a stable reduced Schiff base. Anhydrous salts of chromium (III) nitrate were then added in a 1:2 molar ratio with the reduced Schiff base and stirred overnight to ensure full reaction, forming a light red solution of reduced Schiff base complexes containing nitrate anion. In some experiments, sodium sulfate was then added in a 1:2 molar ratio with the chromium complexes for anion substitution, forming a wine red solution; in other experiments, sodium phosphate was then added in a 1:3 molar ratio with the chromium complexes to form the dark purple solution of Cr RSB solution with phosphate anions;

(1): For list of amino acid used and detailed procedures, please refer to appendix (Page X)

4. Results and Discussion

When the anion of the compound is nitrate, bromine or iodine, the colour of the solution is a wine red color. However, when the anion of the compound is phosphate ion (PO_4^{3-}), the color of the solution was observed to be purple (Figure 3, appendix). The unexpected color change is confirmed by UV-vis spectrometry for all the different variations of amino acid used (Annex part IV), which showed a general shift of the maximal wavelengths of light absorbed (λ_{max}) towards 800 nm for the compounds containing phosphate anion as compared to the compounds with sulfate anion. The anions added are colorless both in solution and in the solid powder form (Figure 2, appendix), hence it can be deduced that the color change of the solution may be due to a structural change in the Chromium reduced Schiff Base complexes .

5. Future work

The solutions of Cr RSB complexes will be crystallized for X-ray diffraction to be carried out and the data of Cr RSB complexes with phosphate anions can be compared with the experimental data of the complexes with sulfate anions to find out about the properties of the compound, and thus explore possible industrial and biological application of the physical properties of the complexes synthesized.

b) Homemade detergents

Abstract
In light of an increase in COVID-19 cases, the Phase 2 (Heightened Alert) was implemented in June 2021. As such, students were temporarily restricted from using the laboratories in the Science Research Centre. In order to ensure that the Project Work journey would continue to be enriching, another project about biological cleaners was carried out. Though chemical cleaners are still dominating the shelves in the supermarkets, homemade fruit peel cleaners have risen in popularity due to their environmentally-friendliness and their ease of production. As such, this project will investigate the effectiveness of these biological cleaners. Varying amounts of ingredients were added and the solutions were fermented over 21 days, after which they were tested on different dirt stains and compared against the effectiveness of water.

1. Introduction
Chemical detergents are used by many people to clean various appliances such as cutlery. However, such high usage of chemical detergents have caused huge damages to our environment. Many chemical detergents contain phosphates which enter the environment via wastewater, acting as nutrients to algae and cause their excessive growth in water bodies, leading to eutrophication of water bodies and depletion of oxygen in the water, which can be fatal to aquatic organisms [6]. Surfactant detergents washed into water bodies can lower surface tension of the water affecting aquatic plants as transpiration may not occur as effectively [7]. Furthermore, some compounds in the detergent may be non-biodegradable [8], which can accumulate in organisms that feed on contaminated food sources in the environment. Hence, even though chemical detergents are effective, they are not environmentally friendly. On the other hand, food wastage has become a pertinent concern in society, with Singapore alone having 665 000 tonnes of food waste generated in 2020 [9]. To alleviate both issues, homemade fruit peel cleaners have risen

in popularity in recent years due to its convenient and quick-to-prepare nature [10], and some were even shown to have an active antimicrobial effect [11].

2. Solution Design

Recipes for fruit peel cleaners were researched online and used as a guide for modification [12]. In the experiments, orange peels, (yeast), sugar and water were mixed in varying amounts in pop bottles. After which, the bottle cap was removed once per day for 3 weeks to release carbon dioxide gas from fermentation. The methods shown online were then investigated to test if they were effective in removing different types of stains on plates.

3. Methods

Orange peels were washed and chopped into pieces small enough to enter a pop bottle. The bottle was then closed tightly and vigorously shaken to dissolve all sugar. For three weeks, CO_2 gas was released from the bottle three times a day. Besides that, the bottle was shaken daily. After 21 days, the solution is poured through a sieve and the liquid is collected. To test the cleaner, 200cm^3 of enzyme cleaner and 50cm^{3}of water was mixed into a spray bottle. The solution is then used to remove stains on a tile by spraying on the stain 5 times and then using a smooth cloth to wipe the stain with minimal force.

4. Results and discussion

All of the solutions were fermented for 21 days. Table 1 (Pages 7 and 8) shows the efficacy of the fruit peel cleaners in removing dirt stains on homogenous floor tiles. From the testing, it can be seen that the fruit peel cleaners are more efficient than water in removing dirt stains, and that the presence of yeast and the varied ingredients used did not affect the results. The orange peels added were used as a fermentation feedstock by various species of microorganisms to undergo anaerobic fermentation using glucose in the sugar provided, which was ensured by the tight capping of the bottles of fermenting fruit peel solutions. The microorganisms secrete ethanol which contains a hydrophilic hydroxyl head and hydrophobic alkyl tail, allowing it to form micelles with dirt particles, which are immiscible with water, which can then be easily be washed away with water, represented in Figure 2 (Page 7).

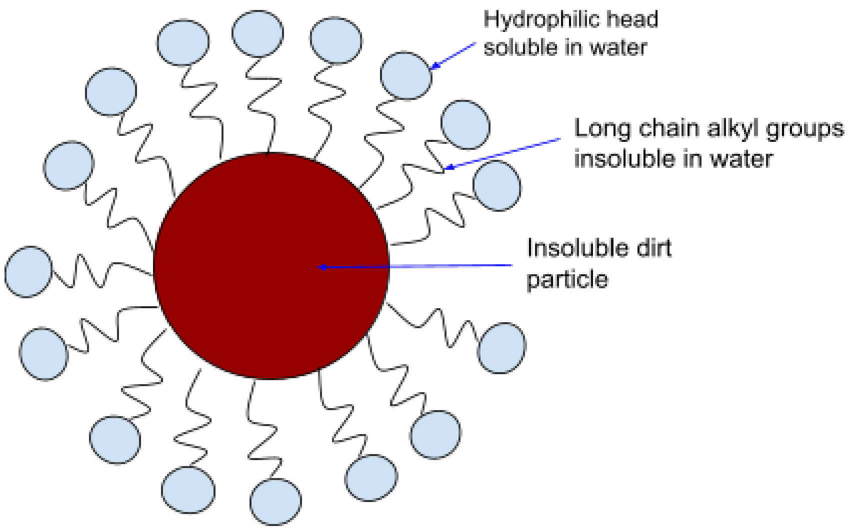
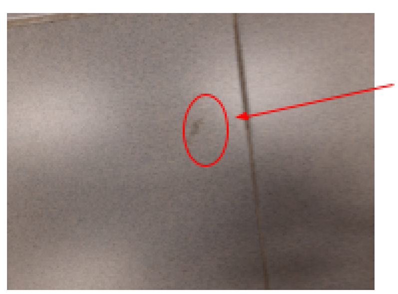
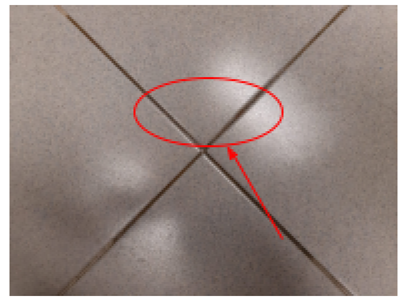
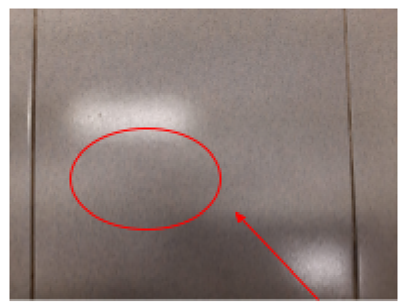


Figure 2 (above): Micelle formed by ethanol produced by the fermentation of orange peels

Hence, it can be concluded that the fruit peel cleaners are highly beneficial as it is effective in cleaning stains, is biodegradable and ecologically friendly, and can cheaply and easily be produced with household objects.

	Before	**After**
Control (Water)		

Normal solution		
Solution with yeast		
Solution with small pieces of orange peels and yeast		

Above: Table 1 showing results of fruit peel cleaners.

5. Future work

Different types of fruit peels can be used for fermentation of different solutions, which can then be used to test on other types of stains such as oil on varying surfaces such as glass and wood. The efficiency of the cleaning of the stains can then be compared and the most efficient formula for the removal of the most cleanable stain and surface can then be investigated.

References:

[1] Warra AA (2011) Transition Metal Complexes And Their Application In Drugs And Cosmetics – A Review J Chem Pharm Res 3(4): 951-958. Retrieved March 8, 2021 from https://www.researchgate.net/publication/215651549_Transition_metal_complexes_and_their_application_in_drugs_and_cosmetics

[2] National Center for Biotechnology Information (2021). PubChem Compound Summary for CID 441203, cis-Platin. Retrieved June 8, 2021 from https://pubchem.ncbi.nlm.nih.gov/compound/cis-Platin

[3] Press, F., & Siever, R. (1986). *Earth.* New York, NY: W.H. Freeman.

[4] Li, B. C., He, J. R., Liu, J. F., & Su, C. Y. (2012, January 17). Anion effect on the structural diversity of three 1D coordination polymers based on a pyridyl diimide ligand. *CrystEngComm* 14, 2152-2158. https://doi.org/10.1039/C2CE06147C

[5] Watson, J., Crick, F. (1953). Molecular Structure of Nucleic Acids: A Structure for Deoxyribose Nucleic Acid. *Nature* 171, 737–738. https://doi.org/10.1038/171737a0

[6] Kogawa, A. C., Cernic, B. G., do Couto, L., & Salgado, H. (2017). Synthetic detergents: 100 years of history. Saudi pharmaceutical journal : SPJ : the official publication of the Saudi Pharmaceutical Society, 25(6), 934–938. https://doi.org/10.1016/j.jsps.2017.02.006

[7] What happens when detergents get into freshwater ecosystems? (n.d.). *Lenntech*. Retrieved July 10, 2021 from https://www.lenntech.com/aquatic/detergents.htm

[8] Scientific Committee on Health and Environmental Risks. (2005, November 25). Opinion on "Environmental Risk Assessment of non Biodegradable Detergent Surfactant under Anaerobic Condition". Retrieved June 15, 2021 from https://ec.europa.eu/health/ph_risk/committees/04_scher/docs/scher_o_021.pdf

[9] National Environment Agency. (n.d.). Food Waste Management. Retrieved July 8, 2021 from https://www.nea.gov.sg/our-services/waste-management/3r-programmes-and-resources/food-waste-management

[10] Wee, L. W. (2016, November 22). Unwanted peels fermented and used to clean. *The Straits Times*. Retrieved 23 June, 2021 from https://www.straitstimes.com/lifestyle/home-design/turn-fruit-peel-into-a-cleaner

[11] Geetha, Saramanda & Kaparapu, Jyothi. (2017, November). Antimicrobial Activity of Fermented Citrus Fruit Peel Extract. 25-28. Retrieved July 13, 2021 from https://www.researchgate.net/publication/341992091_Antimicrobial_Activity_of_Fermented_Citrus_Fruit_Peel_Extract

[12] How to Make Enzyme Cleaner (2021, June 29). wikiHow. Retrieved 9 June, 2021 from https://www.wikihow.com/Make-Enzyme-Cleaner

6. Appendix (Chromium Reduced Schiff Bases)

I. Synthesis of Amino Acid Reduced Schiff Bases

Amino acid (10.0 mmol) was dissolved in water (10 mL) containing excess KOH (0.561g - 0.627g, ≈10.0 mmol). 2-pyridinecarboxaldehyde (0.951mL, 10.0 mmol) was then pipetted into the aqueous solution and stirred in an iced water bath for 45 mins. Excess $NaBH_4$ (0.454 g, 12 mmol) was then added slowly to the solution and stirred until the color of the solution changed from brownish-yellow to light yellow. CH_3CO_2H was added dropwise to the solution to adjust the pH to around 5, removing excess OH^- and BH_4^- ions in the solution.

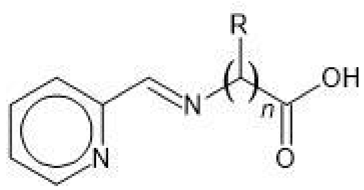
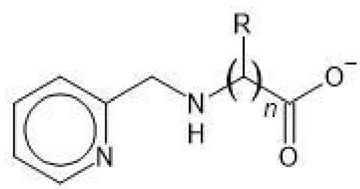
 Schiff base R=H, CH_3 or $CH(CH_3)_2$ n=1 or 2	 Reduced Schiff base ligand R=H, CH_3 or $CH(CH_3)_2$ n=1 or 2

Table 2: Structures of Schiff base and reduced Schiff base ligand

II. Synthesis of Chromium (III) Reduced Schiff Base Complexes

To an aqueous solution of the respective reduced Schiff Bases (10.0 mmol), $Cr(NO_3)_3 \cdot 9H_2O$ (2.00g, 5 mmol) was added and the resulting solution stirred for 24h to form a wine red solution.

III. Counterion Substitution of Chromium (III) Complexes

To an aqueous solution of chromium (III) complexes (5 mmol), sodium phosphate (0.273g, 1.67 mmol) was added and the resulting solution stirred for 24h to form a dark purple solution.

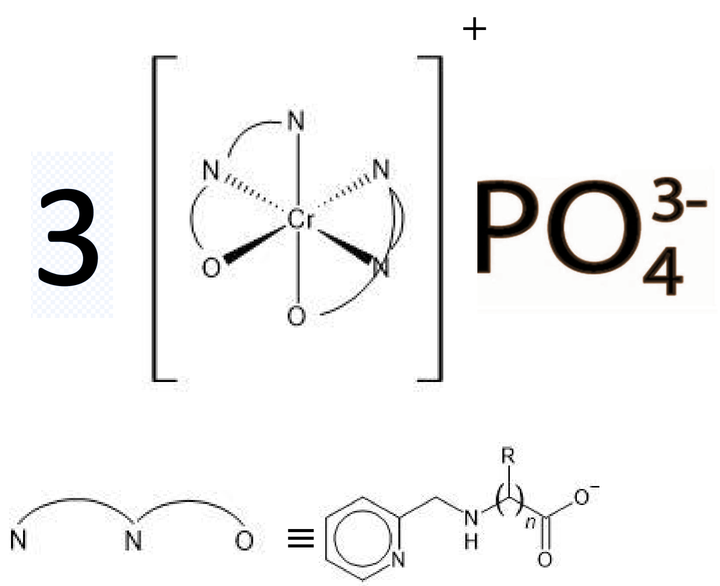
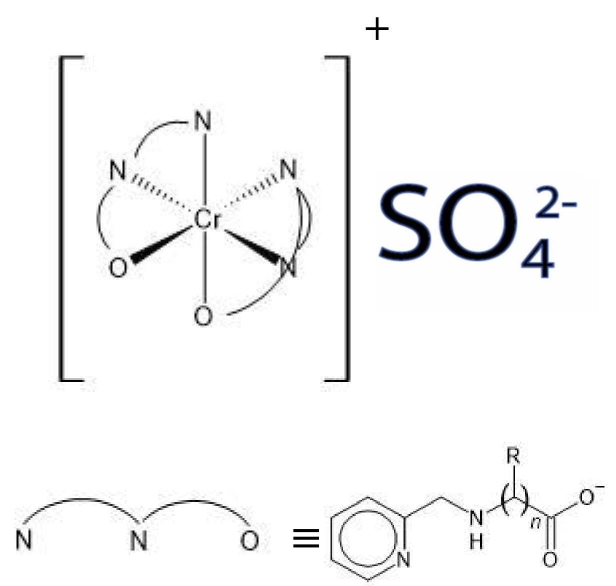
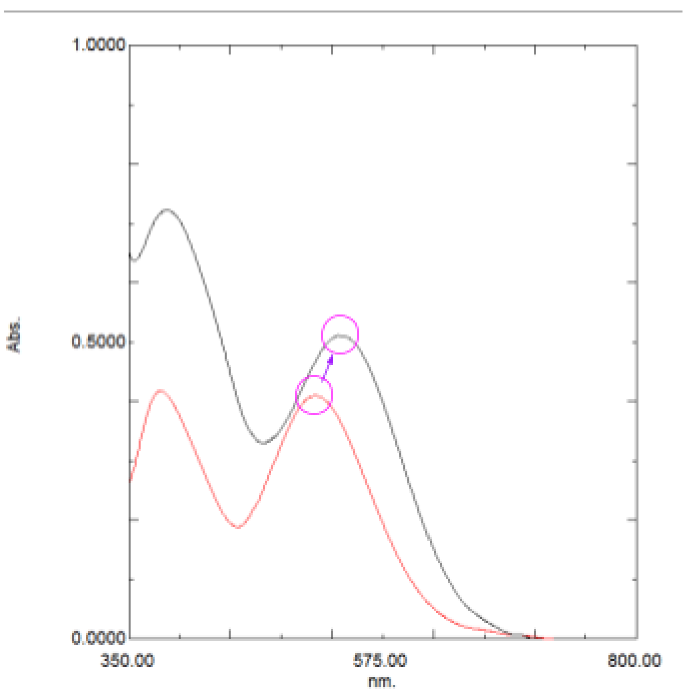
Chromium complexes with PO_4^{3-} anions	Chromium complexes with SO_4^{2-} anion
	

Table 3(above): Structures of Chromium complexes with nitrate and phosphate anions

IV. UV-vis spectrometry results for Cr RSB complexes



Red represents UV-vis results of L-valine derived RSB complexes containing sulfate anion while black represents complexes containing phosphate anion. Purple arrow shows shifting of Second (circled) to the right.

Figure 3, continued: Second λ_{max} shifted from 523 nm to 529 nm when phosphate was substituted.

Figure 3(above): UV-vis graphs for Cr complexes with RSB derived from L-valine:

Amino Acid	Anion	First λ_{max} /nm	Second λ_{max} /nm	Wavelength of light absorbed	Wavelength of light transmitted
Glycine	Sulfate	377	508	508 nm	633 nm
	Phosphate	380	542	542 nm	737 nm
L-Alanine	Sulfate	384	523	523 nm	686 nm
	Phosphate	380	529	529 nm	716 nm
DL-Alanine	Sulfate	395	525	525 nm	704 nm
	Phosphate	398	548	548 nm	743 nm
Beta-Alanine	Sulfate	384	515	515 nm	675 nm
	Phosphate	389	525	525 nm	704 nm
L-Valine	Sulfate	380	520	520 nm	700 nm
	Phosphate	384	532	532 nm	726 nm
DL-Valine	Sulfate	394	528	528 nm	708 nm
	Phosphate	395	538	538 nm	734 nm

Table 4(above): Maximal absorbance wavelengths for the synthesized Chromium amino acid reduced Schiff base complexes

V. Image gallery

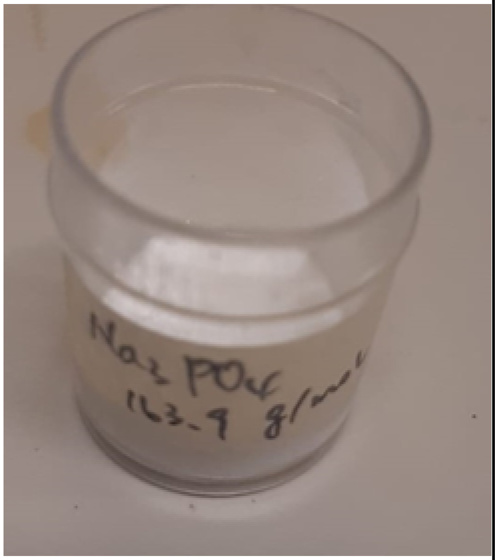
 White powder of sodium phosphate that was added into solution of Cr RSB complexes.	 Sodium phosphate powder dissolves to form a colorless solution in solvent used for Cr RSB (water).

Figure 4 (above): colorless phosphate anions in solution and solid form

 Cr RSB solution containing nitrate anion showing wine-red color	 Cr RSB solution upon addition of sodium phosphate showing purple color

Figure 5 (above): Upon substitution of anion to phosphate, color change of solution was observed after a day.

<u>END OF WRITTEN REPORT</u>