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CRITICAL REVIEWS ON STABILITY AND PHOTOSENSITIZER POTENTIAL OF METAL HEXACYANOFERRATE (II) COMPLEXES: A POSSIBLE PREBIOTIC MINERAL

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ABSTRACT

Bismuth, cadmium, cobalt, manganese, nickel, lead, antimony and zirconium hexacyanoferrate (II) complexes or metal ferrocyanides were synthesized and characterized by elemental and spectral studies. Stability of metal hexacyanoferrate (II) complexes were recorded in heat, light (UV, VIS), different concentrations of various acids (HCl, H_2SO_4, HNO_3), different concentration of various bases (NaOH, KOH, NH_4OH), sea and tap water.The photosensitizing activity of metal hexacyanoferrate (II) complexes were tested by using potassium iodide and starch solution. Nickel, antimony and zirconium ferrocyanides were found to be possible photosensitizer during the course of chemical evolution on primitive Earth.

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RESUMEN

Spanish title*; Revisiones críticas sobre la estabilidad y el potencial fotosensibilizante de complejos metálicos de hexacianoferrato (II): un posible mineral prebiótico*. Los complejos de hexacianoferrato (II) o ferrocianuros metálicos de bismuto, cadmio, cobalto, manganeso, níquel, plomo, antimonio y zirconio fueron sintetizados y caracterizados por estudios espectrales elementales. La estabilidad de los complejos metálicos de hexacianoferrato (II) fue registrada bajo condiciones de calor, luz (UV, VIS), diferentes concentraciones de varios ácidos (HCl, H_2SO_4, HNO_3), diferentes concentraciones de varias bases (NaOH, KOH, NH_4OH), y agua de mar y agua potable. La actividad fotosensibilizadora de los complejos metálicos fue probada mediante el uso de yoduro de potasio y solución de almidón. Los ferrocianuros de niquel, antimonio y zirconio fueron determinados como posibles fotosensibilizadores durante el curso de la evolución química en la era terrestre primitiva.

INTRODUCTION

Due to the ease of formation of cyanide ions under prebiotic conditions, it is thought that cyanide may have formed stable complexes with abundant transition metal ions present in the primeval seas. The primitive Earth was anoxygenic and its reducing potential was not high enough hence most metals were present in their lower oxidation states. It is further assumed that during the course of chemical evolution, cyanide may also have formed some insoluble double metal ferrocyanides of general formula M_2 [Fe $(CN)_6$] x H_2O, where M can be Cd, Sb, Zn, Bi, Cu, Mo etc. The double metal ferrocyanides are insoluble in water and are considered to have settled to the bottom of the primeval sea and acted as active surfaces for the condensation of amino acids nucleic acids, sugars etc. [1]. It is assumed that chemical evolution took place in the primeval sea and their presence was probable. The occurrence of ferri-ferrocyanide in the anoxic Archaean hydrosphere lends support to this hypothesis [2].It is believed that photocatalytic activity by inorganic minerals could have been very pronounced on the primitive Earth. The oxides of titanium, zinc and tungsten possess high photosensitizing activity comparable with the activity of porphyrins and chlorophylls. These compounds are able to sensitize reactions accompanied by light energy storage in terminal stable products [3, 4]. It is well established that metal ferrocyanides act as adsorbents [5-7] ion exchangers [8-11] and photosensitizers [12, 13]. Stability of double metal ferrocyanides in the primeval seas may possibly have played a significant role in the protection and condensation of bioorganic molecules during course of chemical evolution on primitive Earth.

A search in the literature indicated some reports available on synthesis of metal ferrocyanides and very few information available on stability and photosensitizing activity of metal ferrocyanides. In view of this, the attempt was made to study stability and photosensitizing activity of bismuth, cadmium, cobalt, manganese, nickel, lead, antimony and zirconium ferrocyanides.In addition, the present work describes a review on stability and photosensitizing activity of metal ferrocyanides.

RESULTS AND DISCUSSION

Elemental analysis and spectral studies of metal ferrocyanides

The percentage composition of metals in metal ferrocyanides are given in Table 1. The percentage of metals (bismuth, cadmium, cobalt, manganese, nickel, lead, antimony, zirconium) are found higher in comparison to iron. Infrared spectral data of metal ferrocyanides are given in Table 2. Absorption frequencies of water molecule and OH groups are found to be higher than HOH bending and $C \equiv$ N stretching frequencies.

Effects of heat on the stability of metal ferrocyanides

It is clear from Table 3 that bismuth, manganese, cobalt and cadmium ferrocyanides are found to be stable at 100° C. Antimony and zirconium ferrocyanides are stable to heat at 150° C.

Stability of metal ferrocyanides in various concentrations of acids at room temperature and at boiling temperature

It is observed from Table 4 that ferrocyanides of bismuth, nickel and cadmium are insoluble in various concentrations of hydrochloric acid at room temperature with no change in colour. Ferrocyanides of lead, manganese, cobalt, antimony and zirconium are found to be slightly soluble and unstable in various concentration of HCl at room temperature. Table 5 showed that ferrocyanides of nickel, cadmium and lead are insoluble in various concentrations of boiled hydrochloric acid, and they were found to be stable too. Ferrocyanides of cobalt, antimony, zirconium, bismuth and ferrocyanide of manganese are found to be slightly soluble and unstable in various concentrations of boiled hydrochloric acid.

It is clear from Tables 6 and 7 that ferrocyanides of nickel, cobalt, zirconium, cadmium, lead and bismuth are insoluble and stable while ferrocyanides of manganese and antimony are slightly soluble and unstable in various concentrations of sulphuric acid at room temperature and at boiling temperature.

It is observed from Table 8 that ferrocyanides of bismuth, cadmium, cobalt, nickel, lead and zirconium are found to be insoluble and stable while ferrocyanides of antimony and manganese are found to be slightly soluble and unstable in various concentrations of nitric acid at room temperature.

Table 9 showed that cadmium ferrocyanides is found to be stable and insoluble in comparison to ferrocyanides of bismuth, cobalt, manganese, nickel, lead, antimony and zirconium in various concentrations of nitric acid at boiling temperature. The colour changes of metal ferrocyanides may be due to electronic transition in the molecules of the solid metal ferrocyanides.

Stability of metal ferrocyanides in various concentration of bases at room and boil temperature

It is clear from Table 10 that ferrocyanides of bismuth, cadmium, cobalt, manganese, nickel, and zirconium are insoluble and stable while ferrocyanides of antimony and lead are slightly soluble and unstable in various concentrations of sodium hydroxide at room temperature. Table 11 indicated that ferrocyanides of bismuth, cadmium, cobalt, nickel, manganese and zirconium are found to be insoluble and stable while ferrocyanides of antimony and lead are soluble and unstable in various concentration of sodium hydroxide at boiling temperature. It is observed from Tables 12 and 13 that ferrocyanides of bismuth, cadmium, cobalt, manganese, nickel and zirconium are insoluble and stable while lead ferrocyanides is soluble and unstable in various concentrations of potassium hydroxide at room temperature and at boiling temperatures. Antimony ferrocyanide is insoluble and stable at room temperature while it's partly soluble and unstable at boil temperature of KOH. It is clear from Tables 14 and 15 that ferrocyanides of bismuth, cadmium, cobalt, manganese, nickel, antimony and zirconium ferrocyanide, are insoluble and stable while lead ferrocyanides is soluble and unstable in various concentrations of ammonium hydroxide at room temperature and at boil temperatures. The colour change of metal ferrocyanide is mainly due to electronic transition within metal ferrocyanide molecules.

Stability of metal ferrocyanides in tap water and sea water at room and boiling temperature

Table 16 showed that all metal ferrocyanides are found to be insoluble and stable in the tap water and sea (Atlantic Ocean) water at room and boil temperature. This study supports the hypothesis that metal ferrocyanides are possible insoluble and stable during the course of chemical evolution on primitive Earth. They also play important roles in protection and condensation of bioorganic molecules during the course of chemical evolution in primeval seas.

Effect of light (UV/VIS) on the stability of metal ferrocyanides

It is clear from Tables 17 and 18 that ferrocyanides of antimony, cadmium and zirconium are stable in visible and ultraviolet light until 48 hrs of radiation. Ferrocyanides of bismuth and manganese are found to be stable until 12 hrs in vis and uv light. Ferrocyanides of nickel, cobalt and lead are unstable in visible light at 12, 24, 36 and 48 hrs in visible and ultra violet light.

Test on oxidizing and photosensitizing activity of metal hexacyanoferrate (II) complexes.

Test on oxidizing and photosensitizing activity of metal ferrocyanide in potassium iodide and starch solution indicated ferrocyanides of nickel, antimony and zirconium as possible photosensitizers; ferrocyanides of lead, manganese, cobalt and cadmium as possible oxidizer and bismuth ferrocyanide as both oxidizer and photosensitizer during the course of chemical evolution on primitive Earth.

CONCLUSION

The following conclusions can be drawn from the present study:

1. The stability of ferrocyanides of bismuth, cadmium, cobalt, manganese, nickel, lead, antimony and zirconium was found to be affected by the presence of heat and light and not affected by the presence of sea and tap water at room temperature and at boiling temperature.
2. Stability of ferrocyanides of bismuth, cadmium, cobalt, manganese, nickel, lead, antimony and zirconium is affected by acids and bases at room temperature and at boiling temperature.
3. It was found that ferrocyanides of nickel, antimony and zirconium are possible photosensitizers and that ferrocyanides of lead, manganese, cobalt and cadmium are possible oxidizers during the course of chemical evolution and the origins of life on the primitive Earth.
4. It is also concluded from present study that double metal ferrocyanides are insoluble and stable during the course of chemical evolution on primitive Earth and play significant role in condensation of precursors of early life in primeval seas.

EXPERIMENTAL

Materials

All chemicals used were of AnalaR grade. Potassium ferrocyanide, antimony(II) chloride, cadmium (II) chloride, zirconyl chloride, bismuth (II) chloride, lead(II) chloride, manganese(II) chloride, cobalt(II) chloride, nickel(II) chloride were obtained from BDH Poole, England. All chemicals used without further purification. Solutions were prepared in doubly distilled water.

Synthesis of metal hexacyanoferrate (II) complexes

Metal (bismuth, cadmium, manganese, nickel, lead, antimony and zirconium) hexacyanoferrate (II) complexes were prepared according to method reported by Kourim [14]. Metal hexacyanoferrate (II) complexes were prepared by adding metal chloride (500 ml, 0.1 M) and potassium ferrocyanide (167 ml, 0.1 M) solutions with constant stirring. The reaction mixture was heated on a water bath for 3h and kept as such at room temperature. The precipitate was filtered under vacuum, washed several times with distilled water and dried in an air oven at 60C. The dried product was grounded and sieved to 125 µm particle size.

Cobalt ferrocyanide was synthesized by adding (1 volume, 0.5 M) potassium ferrocyanide and (2.4 volume, 0.3 M) cobalt chloride and kept as such after gently stirring over a period of 30 min at room temperature [15]. The slurry of cobalt ferrocyanide was filtered under vacuum, washed several times with distilled water and dried. The resulting granules were dried and powdered to 125 µm particle size.

Characteristics of metal ferrocyanides

Bismuth, cadmium, cobalt, manganese, nickel, lead, antimony and zirconium ferrocyanides are light blue, white, brown, grey, light green, pale green, blue, and deep blue colours, respectively. These metal ferrocyanides are amorphous insoluble solid and showed no x-ray pattern.

The metal ferrocyanides were characterized on the basis of elemental and spectral studies. The percentage composition of metals was determined by IL – 751 atomic adsorption spectrophotometer [16]. Carbon, hydrogen and nitrogen analysis were carried out by CEST – 118, CHN analyzer. Percentage composition of elements in metal ferrocyanides are given in Table 1.

Infrared spectra of the metal ferrocyanides were recorded in KBr disc on Beckman IR-20 spectrophotometer. All eight metal ferrocyanides show at broad peak at 3450 – 3700 cm^{-1} is characteristics of water molecule and OH group. Also a peak at around 1580 – 1635 cm^{-1} is due to HOH bending. Two sharp peaks, one at 1990 – 2070 cm^{-1} and the other at 580 – 610 cm^{-1} in all metal ferrocyanides are characteristics of cyanide stretching and Fe-C stretching frequencies, respectively [17]. Another sharp band at 440-500 cm^{-1} in all metal ferrocyanides probably shows the presence of metal – nitrogen bond thus indicating a certain degree of polymerization in the products [18, 19] (Table 2).

Stability study on metal hexacyanoferrate (II) complexes

Effect of heat on the stability of metal ferrocyanide

A 20 mg of each metal ferrocyanides were placed in a petri dish. The Petri dishes were then placed in the air oven for 6 hrs at 100° C. This process was repeated at 150° C, 200° C and 250° C to demonstrate the effect of heat on the various metal ferrocyanides. The colour of metal ferrocyanides at various temperatures was observed (Table 3)

Stability of metal ferrocyanides in various concentrations of acids at room and at boiling temperature

The metal ferrocyanides (20 mg) were placed in the test tubes containing 10 ml of each 2.0 M, 1.0 M, 0.5 M and 0.1 M acids (HCl, H_2SO_4, HNO_3).The mixture was agitated for 20 mins at room temperature and observation for any change in colour of metal ferrocyanides was recorded (Tables 4, 6, 8). The same reaction mixture boiled on Bunsen flame for 20 mins and any change in colour of metal ferrocyanides was recorded (Tables 5, 7, 9). This process was repeated for each metal ferrocyanides. The colour change of metal ferrocyanides was recorded.

Stability of metal ferrocyanides in various concentrations of bases at room temperature and at boiling temperature

The metal ferrocyanides (20 mg) were placed in the test tubes containing 10 ml of each 2.0 M, 1.0 M, 0.5 M, 0.1 M bases (NaOH, KOH, NH_4OH). The mixture was agitated for 20 minutes at room temperature and observation for any change in colour of metal ferrocyanides was recorded (Tables 10, 12, 14). The same reaction mixture boiled on Bunsen flame for 20 minutes and any change in colour of metal ferrocyanides was recorded (Tables 11, 13, 15). The process is repeated for each metal ferrocyanides. The colour change of metal ferrocyanides was recorded.

Stability of metal ferrocyanides in tap water and sea water at room temperature and at boiling temperature

The metal ferrocyanides (20 mg) were placed in each test tube containing tap water and sea water. The mixture was then agitated for 1h and observation for a change in colour of metal ferrocyanides was recorded (Table 16). The same reaction mixture boiled on Bunsen Flame for 20 mins and change in colour of metal ferrocyanides was recorded (Table 16)

Effect of light (UV/VIS) on the stability of metal ferrocyanides

A 20 mg of each metal ferrocyanide was placed in a dry Petri dish and the original colour was recorded. A 250 W visible lamp was kept vertically above the sample at a distance of 22 cm. The observations for any change in colour of metal ferrocyanides were recorded at 12, 24, 36 and 48 hrs (Table 17). The same experiment was repeated using a long wave (300-380 nm) ultra violet lamp. The observation of any change in colour of metal ferrocyanides was recorded. (Table 18).

Test on oxidizing and photosensitizing activity of metal hexacyanoferrate (II) complexes.

The oxidizing and photosensitizing capacity of metal hexacyanoferrate (II) complexes were compared by potassium iodide and starch solution. Oxidation of iodide to iodine in presence of starch gives blue colour. One drop of freshly prepared 2.0 % starch solution was added into test tubes (length = 10 cm; internal diameter = 1.30 cm) containing 10 ml of 0.1 M potassium iodide solution. A 25 mg of the metal ferrocyanides were added into each test tube and agitated, observation for any decolourization of blue colour and potassium iodide and starch solution was recorded. The same experiment was repeated using a 250 W, visible lamp, and a long wave UV lamp, which were kept vertically above the test tubes at a distance of 15 cm. Photosensitizers will decolourize the blue colour of potassium iodide and starch solution in the presence of light (-VIS/UV). The oxidizers will decolourize the blue colour of potassium iodide and starch solution in absence of light.

Table 1: *Elemental analysis of metal hexacyanoferrate (II) complexes*

*Metal Ferrocyanides**	*Percentage (%) found*				
	Metal	*Iron*	*Carbon*	*Hydrogen*	*Nitrogen*
BiFc	60.61	8.50	10.80	0.90	12.75
CdFc	41.59	11.50	15.13	1.69	17.37
CoFc	26.60	13.10	15.50	2.71	18.10
MnFc	26.90	13.12	16.30	2.80	18.60
NiFc	31.30	14.80	20.30	1.50	21.40
PbFc	58.02	7.80	9.80	1.27	12.32
SbFc	47.50	12.50	15.25	0.89	17.79
ZrFc	34.66	10.30	12.97	2.90	15.41

* BiFc = Bismuth ferrocyanide; CdFc = Cadmium ferrocyanide; CoFc = Cobalt ferrocyanide;
MnFc = Manganese ferrocyanide; NiFc = Nickel ferrocyanide; PbFc = Lead ferrocyanide;
SbFc = Antimony ferrocyanide; ZrFc = Zirconium ferrocyanide

Table 2: *Infrared spectra data of metal ferrocyanides*

*Metal Ferrocyanides**	*Absorption frequency (cm^{-1})*				
	H_2O molecule OH Group	*HOH bending*	*C ≡ N stretching*	*Fe-C*	*Metal – N**
BiFc	3650	1625	2000	580	500
CdFc	3600	1620	2000	600	490
CoFc	3510	1635	2070	595	460
MnFc	3800	1600	2000	610	500
NiFc	3450	1600	2090	590	440
PbFc	3700	1580	1990	600	490
SbFc	3600	1600	2000	580	490
ZrFc	3600	1600	2000	580	500

* Metal – N band shows degree of Polymerization

Table 3: *Effect of heat on metal ferrocyanides*

Metal ferrocyanides	*Original colour*	*100° C*	*150° C*	*200° C*	*250° C*
BiFc	Light blue	No change	Dark blue	Dark brown	Darker brown
CdFc	White	No change	Light brown	Light brown	Brown
CoFc	Brown	No change	Black	Black	Black
MnFc	Grey	No change	Dark grey	Darker grey	Black
NiFc	Light green	Green	Green	Greenish brown	Black
PbFc	Pale green	Dark surface layer	Dark grey	Darker grey	Brownish grey
SbFc	Blue	No change	No change	Brown	Dark brown
ZrFc	Deep blue	No change	No change	Brown	Dark brown

Amount of metal ferrocyanides used = 20 mg; Time = 6hrs

Table 4: *Stability of metal ferrocyanides in hydrochloric acid at room temperature*

Metal ferrocyanides	*Original colour*	*100° C*	*150° C*	*200° C*	*250° C*
BiFc	Insoluble Light blue	Insoluble Light blue	Insoluble Light blue	Insoluble Light blue	Insoluble Light blue
CdFc	Insoluble White particles remained same	Insoluble White particles remained same	Insoluble White particles remained same	Insoluble White particles remained same	Insoluble White particles remained same
CoFc	Slightly soluble Brown particles turned dark blue	Slightly soluble Brown particles turned dark blue	Slightly soluble Brown particles turned black	Slightly soluble Brown particles turned dark blue	Slightly soluble Brown particles turned dark blue
MnFc	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white
NiFc	Insoluble Light green particles turned to dirty green	Insoluble Light green particles turned to dirty green	Insoluble Light green particles turned to dirty green	Insoluble Light green particles turned to dirty green	Insoluble Light green particles turned to dirty green
PbFc	Slightly soluble Pale green particles turned light blue	Slightly soluble Palegreen particles turned light blue	Slightly soluble Palegreen particles turned light blue	Slightly soluble Palegreen particles turned light blue	Slightly soluble Palegreen particles turned light blue
SbFc	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue
ZrFc	Slightly soluble Deep blue particles turned light blue	Slightly soluble Deep blue particles turned light blue	Slightly soluble Deep blue particles turned light blue	Slightly soluble Deep blue particles turned light blue	Slightly soluble Deep blue particles turned light blue

Amount of metal ferrocyanides used = 20 mg; Volume of hydrochloric acid = 10 ml; Time = 6hrs; Room temperature = 31°C

Table 5: *Stability of metal ferrocyanides in hydrochloric acid at boiling temperature*

Metal ferrocyanides	*2.0M*	*1.0M*	*0.5M*	*0.2M*	*0.1M*
BiFc	Slightly soluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change
CdFc	Insoluble White particles turned pale green	Insoluble White particles turned pale green	Insoluble White particles turned pale green	Insoluble White particles turned pale green	Insoluble White particles turned pale green
CoFc	Slightly soluble Brown particles turned green	Slightly soluble Brown particles turned green	Slightly soluble Brown particles turned green	Slightly soluble Brown particles turned green	Slightly soluble Brown particles turned green
MnFc	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white
NiFc	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change
PbFc	Insoluble Pale green particles did not change	Insoluble Pale green particles did not change	Insoluble Pale green particles did not change	Insoluble Pale green particles did not change	Insoluble Pale green particles did not change
SbFc	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue
ZrFc	Slightly soluble Deep blue particles did not change	Slightly soluble Deep blue particles did not change	Slightly soluble Deep blue particles did not change	Slightly soluble Deep blue particles did not change	Slightly soluble Deep blue particles did not change

Amount of metal ferrocyanides used = 20 mg; Volume of hydrochloric acid = 10 ml; Time = 20 mins; Room temperature = 31°C

Table 6: *Stability of metal ferrocyanides in sulphuric acid at room temperature*

Metal ferrocyanides	*2.0M*	*1.0M*	*0.5M*	*0.2M*	*0.1M*
BiFc	Insoluble Light blue particles, did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change
CdFc	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change
CoFc	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change
MnFc	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white
NiFc	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change
PbFc	Insoluble Pale green particles change to light green	Insoluble Pale green particles change to light green	Insoluble Pale green particles change to light green	Insoluble Pale green particles change to light green	Insoluble Pale green particles change to light green
SbFc	Slightly soluble Blue particles did not change	Slightly soluble Blue particles did not change	Slightly soluble Blue particles did not change	Slightly soluble Blue particles did not change	Slightly soluble Blue particles did not change
ZrFc	Insoluble Deep blue particles turned light green	Insoluble Deep blue particles turned light green	Insoluble Deep blue particles turned light green	Insoluble Deep blue particles turned light green	Insoluble Deep blue particles turned light green

Amount of metal ferrocyanides used = 20 mg; Volume of sulphuric acid = 10 ml; Time = 20 mins; Room temperature = 31°C

Table 7: *Stability of metal ferrocyanides in boiling sulphuric acid*

Metal ferrocyanides	*2.0M*	*1.0M*	*0.5M*	*0.2M*	*0.1M*
BiFc	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change
CdFc	Insoluble White particles turned pale green	Insoluble White particles turned pale green	Insoluble White particles turned pale green	Insoluble White particles turned pale green	Insoluble White particles turned pale green
CoFc	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change
MnFc	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white
NiFc	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change
PbFc	Insoluble Pale green particles changed to light blue	Insoluble Pale green particles changed to light blue	Insoluble Pale green particles changed to light blue	Insoluble Pale green particles changed to light blue	Insoluble Pale green particles changed to light blue
SbFc	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue
ZrFc	Insoluble Deep blue particles turned light green	Insoluble Deep blue particles turned light green	Insoluble Deep blue particles turned light green	Insoluble Deep blue particles turned light green	Insoluble Deep blue particles turned light green

Amount of metal ferrocyanides used = 20 mg; Volume of sulphuric acid = 10 ml; Time = 20 mins; Room temperature = 31°C

Table 8. *Stability of metal ferrocyanides in nitric acid at room temperature*

Metal ferrocyanides	*2.0M*	*1.0M*	*0.5M*	*0.2M*	*0.1M*
BiFc	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change
CdFc	Insoluble White particles turned light green	Insoluble White particles turned light green	Insoluble White particles turned light green	Insoluble White particles turned light green	Insoluble White particles turned light green
CoFc	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change
MnFc	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white	Slightly soluble Grey particles turned white
NiFc	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change
PbFc	Insoluble Pale green particles change to light blue	Insoluble Pale green particles change to light blue	Insoluble Pale green particles change to light blue	Insoluble Pale green particles change to light blue	Insoluble Pale green particles change to light blue
SbFc	Slightly soluble Blue particles did not change	Slightly soluble Blue particles did not change	Slightly soluble Blue particles did not change	Slightly soluble Blue particles did not change	Slightly soluble Blue particles did not change
ZrFc	Insoluble Deep blue particles did not change	Insoluble Deep blue particles did not change	Insoluble Deep blue particles did not change	Insoluble Deep blue particles did not change	Insoluble Deep blue particles did not change

Amount of metal ferrocyanides used = 20 mg; Volume of nitric acid = 10 ml; Time = 20 mins; Room temperature = 31°C

Table 9: *Stability of metal ferrocyanides in boiling nitric acid*

Metal ferrocyanides	*2.0M*	*1.0M*	*0.5M*	*0.2M*	*0.1M*
BiFc	Slightly soluble Light blue change to green	Slightly soluble Light blue change to green	Slightly soluble Blue Green change to green	Slightly soluble Light blue change to green	Slightly soluble Light blue change to green
CdFc	Insoluble White particles turned rust brown	Insoluble White particles turned rust brown	Insoluble White particles turned rust brown	Insoluble White particles turned rust brown	Insoluble White particles turned rust brown
CoFc	Slightly soluble Brown particles did not change	Slightly soluble Brown particles did not change	Slightly soluble Brown particles did not change	Slightly soluble Brown particles did not change	Slightly soluble Brown particles did not change
MnFc	Slightly soluble Grey particles turned rust brown	Slightly soluble Grey particles turned rust brown	Slightly soluble Grey particles turned rust brown	Slightly soluble Grey particles turned rust brown	Slightly soluble Grey particles turned rust brown
NiFc	Slightly soluble Light green particles, turned dirty green	Slightly soluble Light green particles, turned dirty green	Slightly soluble Light green particles, turned dirty green	Slightly soluble Light green particles, turned dirty green	Slightly soluble Light green particles, turned dirty green
PbFc	Soluble Pale green particles dissolved to give a dark yellow solution	Soluble Pale green particles dissolved to give a dark yellow solution	Soluble Pale green particles dissolved to give a dark yellow solution	Soluble Pale green particles dissolved to give a dark yellow solution	Soluble Pale green particles dissolved to give a dark yellow solution
SbFc	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue	Slightly soluble Blue particles turned deep blue
ZrFc	Slightly soluble Deep blue particles change to dark green	Slightly soluble Deep blue particles change to dark green	Slightly soluble Deep blue particles change to dark green	Slightly soluble Deep blue particles change to dark green	Slightly soluble Deep blue particles change to dark green

Amount of metal ferrocyanides used = 20 mg; Volume of nitric acid = 10 ml; Time = 20 mins; Room temperature = 31°C

Table 10: *Stability of metal ferrocyanides in sodium hydroxide solution at room temperature*

Metal ferrocyanides	*2.0M*	*1.0M*	*0.5M*	*0.2M*	*0.1M*
BiFc	Insoluble Light blueparticles change to yellow	Insoluble Light blue particles change to yellow	Insoluble Light blue particles change to yellow	Insoluble Light blue particles change to yellow	Insoluble Light blue particles change to yellow
CdFc	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change
CoFc	Insoluble Brown particles changed to rust brown	Insoluble Brown particles changed to rust brown	Insoluble Brown particles changed to rust brown	Insoluble Brown particles changed to rust brown	Insoluble Brown particles changed to rust brown
MnFc	Insoluble Grey particles changed to light brown	Insoluble Grey particles changed to light brown	Insoluble Grey particles changed to light brown	Insoluble Grey particles changed to light brown	Insoluble Grey particles changed to light brown
NiFc	Insoluble Light green particles change to dirty green	Insoluble Light green particles change to green	Insoluble Light green particles change to green	Insoluble Light green particles change to green	Insoluble Light green particles change to green
PbFc	Slightly soluble Pale green particles changed to white	Slightly soluble Pale green particles changed to white	Slightly soluble Pale green particles changed to white	Slightly soluble Pale green particles changed to white	Slightly soluble Pale green particles changed to white
SbFc	Slightly soluble Blue particles changed to brown	Slightly soluble Blue particles changed to brown	Slightly soluble Blue particles changed to brown	Slightly soluble Blue particles changed to brown	Slightly soluble Blue particles changed to brown
ZrFc	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown

Amount of metal ferrocyanides used = 20 mg; Volume of sodium hydroxide = 10 ml; Time = 20 mins; Room temperature = 31°C

Table 11: *Stability of metal ferrocyanides in boiling sodium hydroxide*

Metal ferrocyanides	*2.0M*	*1.0M*	*0.5M*	*0.2M*	*0.1M*
BiFc	Insoluble Light blue particles change to yellow	Insoluble Light blue particles change to yellow	Insoluble Light blue particles change to yellow	Insoluble Light blue particles change to yellow	Insoluble Light blue particles change to yellow
CdFc	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change
CoFc	Insoluble Brown particles changed to rust brown	Insoluble Brown particles changed to rust brown	Insoluble Brown particles changed to rust brown	Insoluble Brown particles changed to rust brown	Insoluble Brown particles changed to rust brown
MnFc	Insoluble Grey particles changed to rust brown	Insoluble Grey particles changed to rust brown	Insoluble Grey particles changed to rust brown	Insoluble Grey particles changed to rust brown	Insoluble Grey particles changed to rust brown
NiFc	Insoluble Light green particles change to dark green	Insoluble Light green particles change to dark green	Insoluble Light green particles change to dark green	Insoluble Light green particles change to dark green	Insoluble Light green particles change to dark green
PbFc	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved
SbFc	Partly soluble Blue particles turned yellow	Partly soluble Blue particles turned yellow	Partly soluble Blue particles turned yellow	Partly soluble Blue particles turned yellow	Partly soluble Blue particles turned yellow
ZrFc	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown

Amount of metal ferrocyanides used = 20 mg; Volume of sodium hydroxide used= 10 ml; Time = 20 mins; Room temperature = 31°C

Table 12: *Stability of metal ferrocyanides in potassium hydroxide at room temperature*

Metal ferrocyanides	*2.0M*	*1.0M*	*0.5M*	*0.2M*	*0.1M*
BiFc	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow
CdFc	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change
CoFc	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change
MnFc	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown
NiFc	Insoluble Light green particles change dark green	Insoluble Light green particles change dark green	Insoluble Light green particles change dark green	Insoluble Light green particles change dark green	Insoluble Light green particles change dark green
PbFc	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved
SbFc	Insoluble Blue particles did not change	Insoluble Blue particles did not change	Insoluble Blue particles did not change	Insoluble Blue particles did not change	Insoluble Blue particles did not change
ZrFc	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown

Amount of metal ferrocyanides used = 20 mg; Volume of sodium hydroxide used= 10 ml; Time = 20 mins; Room temperature = 31°C

Table 13: *Stability of metal ferrocyanides in boiling potassium hydroxide*

Metal ferrocyanides	*2.0M*	*1.0M*	*0.5M*	*0.2M*	*0.1M*
BiFc	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow
CdFc	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change
CoFc	Insoluble Brown particles turned rust brown	Insoluble Brown particles turned rust brown	Insoluble Brown particles turned rust brown	Insoluble Brown particles turned rust brown	Insoluble Brown particles turned rust brown
MnFc	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown
NiFc	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green
PbFc	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved
SbFc	Partly soluble Some blue particles dissolved	Partly soluble Some blue particles dissolved	Partly soluble Some blue particles dissolved	Partly soluble Some blue particles dissolved	Partly soluble Some blue particles dissolved
ZrFc	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown

Amount of metal ferrocyanides used = 20 mg; Volume of potassium hydroxide= 10 ml; Time = 20 mins; Room temperature = 31°C

Table 14: *Stability of metal ferrocyanides in ammonium hydroxide at room temperature*

Metal ferrocyanides	*2.0M*	*1.0M*	*0.5M*	*0.2M*	*0.1M*
BiFc	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow
CdFc	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change
CoFc	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change
MnFc	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown
NiFc	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green
PbFc	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved
SbFc	Insoluble Blue particles did not change	Insoluble Blue particles did not change	Insoluble Blue particles did not change	Insoluble Blue particles did not change	Insoluble Blue particles did not change
ZrFc	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles, changed to light brown	Insoluble Deep blue particles changed to light brown

Amount of metal ferrocyanides used = 20 mg; Volume of ammonium hydroxide= 10 ml; Time = 20 mins; Room temperature = 31°C

Table 15: *Stability of metal ferrocyanides in boiling ammonium hydroxide*

Metal ferrocyanides	*2.0M*	*1.0M*	*0.5M*	0.2M	*0.1M*
BiFc	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow	Insoluble Light blue particles turned yellow
CdFc	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change
CoFc	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change
MnFc	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown	Insoluble Grey particles turned rust brown
NiFc	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green	Insoluble Light green particles turned dark green
PbFc	Soluble Pale green particlesdissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved	Soluble Pale green particles dissolved
SbFc	Insoluble Blue particles did not change	Insoluble Blue particles did not change	Insoluble Blue particles did not change	Insoluble Blue particles did not change	Insoluble Blue particles did not change
ZrFc	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown	Insoluble Deep blue particles changed to light brown

Amount of metal ferrocyanides used = 20 mg; Volume of ammonium hydroxide= 10 ml; Time = 20 mins; Room temperature= 31°C

Table 16: *Stability of metal ferrocyanides in sea and tap water (boiled and room temperature)*

Metal ferrocyanides	*Sea water Room Temp*	*Sea Water Boiled*	*Tap Water Room Temp*	*Tap Water Boiled*
BiFc	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change	Insoluble Light blue particles did not change
CdFc	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change	Insoluble White particles did not change
CoFc	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change	Insoluble Brown particles did not change
MnFc	Insoluble grey particles did not change	Insoluble grey particles did not change	Insoluble grey particles did not change	Insoluble grey particles did not change
NiFc	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change	Insoluble Light green particles did not change
PbFc	Insoluble Pale green particles did not change	Insoluble Pale green particles did not change	Insoluble Pale green particles did not change	Insoluble Pale green particles did not change
SbFc	Insoluble Blue particles did not change	Insoluble Blue particles did not change	Insoluble Blue particles did not change	Insoluble Blue particles did not change
ZrFc	Insoluble Deep blue particles did not change	Insoluble Deep blue particles did not change	Insoluble Deep blue particles did not change	Insoluble Deep blue particles did not change

Amount of metal ferrocyanides used = 20 mg; Volume of sea and tap water used= 10 ml; Time = 20 mins; Room temperature = 31°C

Table 17: *Effect of light (VIS) on the stability of metal ferrocyanides*

Metal ferrocyanides	*Original colour*	*12 hrs*	*24 hrs*	*36 hrs*	*48 hrs*
BiFc	Light blue	No change	Dark blue	Dark blue	Darker blue
CdFc	White	No change	No change	No change	No change
CoFc	Brown	Dark brown	Dark brown	Dark brown	Dark brown
MnFc	Grey	No change	Dark grey	Dark grey	Darker grey
NiFc	Light green	Green	Green	Green	Green
PbFc	Pale green	Dark light green	Dark light green	Dark light green	Dark light green
SbFc	Blue	No change	No change	No change	No change
ZrFc	Deep blue	No change	No change	No change	No change

Amount of metal ferrocyanides used = 20 mg; Lamp = 250 watt, VIS; Distance of lamp from metal ferrocyanides = 22 cm

Table 18: *Effect of light (UV) on the stability of metal ferrocyanides*

Metal ferrocyanides	*Original colour*	*12 hrs*	*24 hrs*	*36 hrs*	*48 hrs*
BiFc	Light blue	No change	Dark blue	Dark blue	Darker blue
CdFc	White	No change	No change	No change	No change
CoFc	Brown	Dark brown	Dark brown	Dark brown	Dark brown
MnFc	Grey	No change	Dark grey	Dark grey	Darker grey
NiFc	Light green	Green	Green	Green	Green
PbFc	Pale green	Dark light green	Dark light green	Dark light green	Dark light green
SbFc	Blue	No change	No change	No change	No change
ZrFc	Deep blue	No change	No change	No change	No change

Amount of metal ferrocyanides used = 20 mg; Lamp = 250 watt, UV, Long wave (300-380 nm); Distance of lamp from metal ferrocyanides = 22 cm

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