



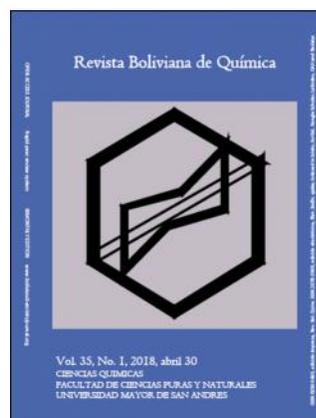
**CRITICAL REVIEWS ON STABILITY
AND PHOTSENSITIZER POTENTIAL
OF METAL FERROCYANIDES: A
POSSIBLE PREBIOTIC MINERAL;
PART (II)**

**REVISIONES CRÍTICAS SOBRE LA
ESTABILIDAD Y EL POTENCIAL
FOTOSENSIBILIZANTE DE LOS
FERROCIANUROS METÁLICOS: UN
POSIBLE MINERAL PREBIOTICO;
PARTE (II)**

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ABSTRACT

Aluminum, barium, chromium, indium, platinum, stannous and vanadium ferrocyanides were synthesized and characterized by elemental analysis and spectral studies. Stability of synthesized metal ferrocyanides were recorded in heat, light (UV, VIS), various concentrations of acids (HCl, H₂SO₄), various concentrations of bases (NaOH, KOH, NH₄OH), sea water and from faucet at room and boil temperature. Stability of synthesized metal ferrocyanides was also recorded in organic solvents (ether, acetone, ethanol, formaldehyde) at room temperature. The oxidizing and photosensitizing potential of synthesized metal ferrocyanides were tested using potassium iodide and freshly prepared starch solution. The hexacyanoferrate (II) complexes of chromium, indium and platinum were found to be possible oxidizer and photosensitizer during the course of chemical evolution on primitive earth.

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RESUMEN



Los ferrocianuros de aluminio, bario, cromo, indio, platino, estannoso y vanadio se sintetizaron y caracterizaron mediante análisis elemental y estudios espectrales. La estabilidad de los ferrocianuros metálicos sintetizados se registró en calor, luz (UV, VIS), diversas concentraciones de ácidos (HCl, H₂SO₄), diversas concentraciones de bases (NaOH, KOH, NH₄OH), agua de mar y del grifo a temperatura ambiente y de ebullición. La estabilidad de los ferrocianuros metálicos sintetizados también se registró en disolventes orgánicos (éter, acetona, etanol, formaldehído) a temperatura ambiente. El potencial oxidante y fotosensibilizador de ferrocianuros metálicos sintetizados se analizaron usando yoduro de potasio y solución de almidón recién preparada. Los complejos de hexacianoferrato (II) de cromo, indio y platino se encontraron como posibles oxidantes y fotosensibilizadores durante el curso de la evolución química en la tierra primitiva.

INTRODUCTION

Since the classic experiments of Miller [1], it is believed that the origin of life processes began with the formation of biomonomers such as aminoacids, pentose sugars, nucleotides, purine and pyrimidine. It has also been proposed that main steps in the origin of life must have involved the formation of important biopolymers from biomonomers in primeval seas, but it is not well established as to how the bio-monomers have concentrated from dilute aqueous solution and polymerized to give large complex molecules. It is assumed that clay minerals and large metal oxides available near sea shores might have played a key role in concentration of biomonomers through adsorption and desorption processes on their surfaces. The importance of clay minerals in chemical evolution was first proposed by Bernal in 1951 and proposed that clays near the hydrosphere-lithosphere interface might have adsorbed micro-biomonomers on and between their silicate layers facilitating thus the condensation considerably, leading to the formation of biopolymers and protecting them against hydrolysis [2].

It is assumed that divalent transition metal ions which were in abundance in the primeval sea would have formed complexes with the simple molecules readily available to them [3,4]. It is therefore, assumed that transition metal ions could easily have formed a number of soluble and insoluble complexes with the abundant CN⁻, in the primeval sea. The insoluble cyanometal complexes thus formed could have settled at the bottom of the sea or at the seashore and might have catalyzed a number of reactions like condensation-oligomerization, oxidation and interaction reactions on their surfaces. The existence of ferriferrocyanide and metal ferrocyanides on the primitive earth has been reported by Arrhenius [5]. Activity of metal ferrocyanides as adsorbents [6, 7], ion-exchangers [8-10] and photosensitizes [11-13] is well established. The lower valent metal ions substituted in potassium ferrocyanide provide a good adsorption site that could have played an important role in chemical evolution and prebiotic chemistry. The insoluble double metal ferrocyanides, either settled at the bottom of the sea or on the seashore, on coming in contact with biomolecules could have acted as active surfaces for concentrating them.

A search for literature indicated some reports available on synthesis of metal hexacyanoferrate (II) complexes and very few report available on stability and photosensitizing activity of metal hexacyanoferrate (II). In view of this, attempt was made to study stability and photosensitizing activity of the aluminum, barium, chromium, indium, platinum, stannous and vanadium hexacyanoferrate (II) complexes. In addition, the present work describes a critical review on stability and photosensitizing potential of aluminum, barium, chromium, indium, platinum, stannous and chromium hexacyanoferrate (II) complexes.

RESULTS AND DISCUSSION

Elemental analysis of metal hexacyanoferrate (II) complexes

The percentage compositions of metals in metal hexacyanoferrate (II) complexes are given in Table 1. The percentage of metals (aluminum, barium, chromium, indium, platinum, stannous and vanadium) are found higher in comparison to iron in all complexes of hexacyanoferrate (II) studied. It is also clear from Table 1 that percentage of hydrogen is lowest in comparison to other elements in each metal ferrocyanides studied. The greater the percentage of hydrogen more the water molecules are expected to attached to metal hexacyanoferrate (II) complexes.

Spectral studies of metal hexacyanoferrate (II) complexes

The infrared special data of hexacyanoferrate (II) complexes are given in Table 2. It is observed from Table 2 that water molecules/OH groups and metal-nitrogen band shows highest and lowest absorption frequencies, respectively. The HOH bending C=N stretching and Fe-C stretching frequencies are observed around 1600 cm⁻¹, 2000 cm⁻¹ and 600cm⁻¹, respectively.



Effect of heat on the stability of metal hexacyanoferrate (II) complexes

It is clear from Table 3 that hexacyanoferrate (II) complexes of indium and platinum are stable at 100°C, while those of aluminum, barium, stannous and chromium platinum are unstable at 100°C.

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

MFCs	Percentage (%) found				
	Metal	Iron	Carbon	Hydrogen	Nitrogen
AlFc	19.90	11.10	13.20	4.90	16.60
BaFc	20.10	9.25	12.80	1.60	15.80
CrFc	10.80	8.50	14.86	3.23	16.15
InFc	49.60	8.46	12.20	1.80	15.75
PtFc	57.15	8.25	10.00	1.30	12.60
SnFc	38.75	10.90	14.25	1.75	18.10
VaFc	24.10	13.90	18.10	2.00	19.73

MFCs = Metal hexacyanoferrate(II) complexes

AlFc = Aluminum hexacyanoferrate (II)

BaFc = Barium hexacyanoferrate (II)

CrFc = Chromium hexacyanoferrate (II)

VaFc = Vanadium hexacyanoferrate (II)

InFc = Indium hexacyanoferrate (II)

PtFc = Platinum hexacyanoferrate (II)

SnFc = Stannous hexacyanoferrate (II)

Table 2: Infrared spectra data of metal hexacyanoferrate (II) complexes

MFCs	Absorption frequency (cm ⁻¹)				
	H ₂ O molecule /OH groups	HOH bending	C=N stretching	Fe-C stretching	Metal-N*
AlFc	3600	1660	2000	600	490
BaFc	3350	1570	1990	590	500
CrFc	3700	1600	2040	590	500
InFc	3040	1510	2000	580	480
PtFc	3510	1590	2000	600	500
SnFc	3600	1600	2000	600	500
VaFc	3600	1600	2040	600	500

MFCs = Metal hexacyanoferrate(II) complexes

*Metal-nitrogen bond show degree of polymerization

Table 3: Effect of heat on the stability of metal complexes of hexacyanoferrate (II)

MFCs	Original Color	100°C	150°C	200°C	250°C
AlFc	Light blue	Blue	Dark blue	Dark blue	Black
BaFc	Pale greenish white	White	pale bluish white	pale bluish white	pale bluish white
CrFc	Bright green	Dark green	Dark green	Black	Dark brown
InFc	Light blue	Light blue	Blue	grey	grey
PtFc	Dark blue	Dark blue	Black	Brown	Brown
SnFc	Blue	Dark blue	Dark blue	Dark blue	Black
VaFc	Dark Green	Green	Green	Brown	Brown

MFCs = metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 6 hours



Stability of metal hexacyanoferrate (II) complexes in various concentrations of acids at room temperature and at boiling temperature

It is observed from Table 4 that hexacyanoferrate (II) complexes of aluminum are slightly soluble in various concentrations of hydrochloric acid at room temperature with change in colour. Hexacyanoferrate (II) complexes of barium, stannous and vanadium are insoluble in various concentrations of hydrochloric acid with change in colour at room temperature. Hexacyanoferrate (II) complexes of chromium, indium and platinum are soluble at high concentration of hydrochloric acid (2.0 M), while slightly soluble or insoluble at low concentrations of hydrochloric acid with change in colour at room temperature.

Table 4: *Stability of metal hexacyanoferrate (II) complexes in hydrochloric acid at room temperature*

MFcs (OC)	2.0 M	1.0 M	0.5 M	0.2 M	0.1 M
AlFc (Light blue)	Slightly soluble Particles changed to blue green				
BaFc (Pale greenish white)	Insoluble pale greenish white particles change to black	Insoluble pale greenish white particles change to black	Insoluble pale greenish white particles change to black	Insoluble pale greenish white particles change to green	Insoluble pale greenish white particles change to green
CrFc (Bright green)	Soluble bright green	Slightly soluble dark green	Insoluble dark green	Insoluble dark green	Insoluble dark green
InFc (Light blue)	Soluble light blue	Soluble light blue	Slightly soluble blue	Slightly soluble grey	Slightly soluble grey
PtFc (Dark blue)	Slightly soluble dark blue	Insoluble dark blue	Insoluble dark blue	Insoluble dark blue	Insoluble dark blue
SnFc (Blue)	Insoluble blue particles changed to dark blue				
VaFc (Dark green)	Insoluble dark green particles changed to light green				

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 20 minutes

Volume of acids = 10 mL

Room temperature = 31.0° C

Table 5 shows that hexacyanoferrate (II) complexes of aluminum, stannous, vanadium and chromium are partially soluble in various concentrations of boiling hydrochloric acid with change in colour, while those of indium are soluble at various concentrations of boiling hydrochloric acid and those of barium and platinum are insoluble in various concentrations of boiling hydrochloric acid.

It is observed in Table 6 that hexacyanoferrate (II) complexes of aluminum, stannous, chromium and indium are partially soluble in various concentrations of sulphuric acid at room temperature with change in colour, those of barium, platinum and vanadium are insoluble in various concentrations of sulphuric acid with change in colour at room temperature.



It is clear from Table 7 that hexacyanoferrate (II) complexes of aluminum, stannous, indium and chromium are partially soluble in various concentrations of sulphuric acid at boiled temperature with change in colour, those of barium, platinum and vanadium are insoluble in various concentrations of boiling sulphuric acid with change in colour. The colour change of metal hexacyanoferrate (II) complexes in various acids is mainly due to electronic transition within molecules of metal hexacyanoferrate (II) complex.

Table 5: Stability of metal hexacyanoferrate (II) complexes in hydrochloric acid at boiling temperature

MFcs (OC)	2.0 M	1.0 M	0.5 M	0.2 M	0.1 M
AlFc (Light blue)	Partial soluble blue Particles turn black	Partial soluble blue particles turn black	Partial soluble blue particles turn black	Partial soluble blue particles turn green	Partial soluble blue particles turn green
BaFc (Pale greenish white)	Insoluble green particles turn black				
CrFc (Bright green)	Partially soluble dark green				
InFc (Light blue)	Soluble blue	Soluble blue	Soluble blue	Soluble grey	Soluble grey
PtFc (Dark blue)	Insoluble dark blue				
SnFc (Blue)	Partial soluble blue particles turn black				
VaFc (Dark green)	Partial soluble green particles turn darker				

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 20 minutes

Volume of acids = 10 mL

Room temperature = 31.0°C

Stability of metal hexacyanoferrate (II) complexes in various concentrations of bases at room temperature and at boiled temperature

It is observed from Table 8 that hexacyanoferrate (II) complexes of aluminum, chromium and indium are partially soluble in various concentrations of sodium hydroxide with colour change at room temperature, those of barium, stannous, vanadium and platinum are insoluble in various concentrations of sodium hydroxide with colour change at room temperature.

It is clear from Table 9 that hexacyanoferrate (II) complexes of aluminum and barium are partially soluble in various concentrations of sodium hydroxide with colour change at boiling point, while those of chromium and indium are partially soluble at high concentration of sodium hydroxide and insoluble at low concentration of sodium hydroxide, respectively at boiling temperature, those of stannous, vanadium and platinum are in insoluble in various concentrations of sodium hydroxide at boiling temperature.

Table 10 shows that hexacyanoferrate (II) complexes of aluminum is partially soluble in various concentrations of potassium hydroxide with colour change at room temperature, while those of chromium and indium are partially



soluble at high concentration of potassium hydroxide and insoluble at low concentration of potassium hydroxide, respectively at room temperature, those of barium, stannous, vanadium and platinum are insoluble in various concentrations of potassium hydroxide at room temperature.

Table 6: Stability of metal hexacyanoferrate (II) complexes in sulphuric acid at room temperature

MFcs (OC)	2.0 M	1.0 M	0.5 M	0.2 M	0.1 M
AlFc (Light blue)	Partially soluble blue turn green				
BaFc (Pale greenish white)	Insoluble pale green particles turn brown				
CrFc (Bright green)	Partially soluble dark green				
InFc (Light blue)	Partially soluble blue	Partially soluble blue	Partially soluble blue	Partially soluble grey	Partially soluble grey
PtFc (Dark blue)	Insoluble dark blue				
SnFc (Blue)	Partially soluble blue turn dark				
VaFc (Dark green)	Insoluble green turn brown				

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 20 minutes

Volume of acids = 10 mL

Room temperature = 31.0°C

It is evident from Table 11 that aluminum hexacyanoferrate (II) complexes are partially soluble in various concentrations of potassium hydroxide at boiling temperature, while those of chromium and indium are partially soluble at high concentration of potassium hydroxide and insoluble at low concentration of potassium hydroxide, respectively at boiling temperature, those of barium, stannous, vanadium and platinum are insoluble in various concentrations of potassium hydroxide at boiling temperature.

From Table 12 we observe that aluminum hexacyanoferrate (II) complexes are partially soluble in various concentrations of ammonium hydroxide with colour changes at room temperature, while those of chromium and indium are partially soluble at high concentration of ammonium hydroxide and insoluble at low concentration, respectively at room temperature, those of barium, stannous, vanadium and platinum are insoluble in various concentrations of ammonium hydroxide at room temperature.

Table 13 shows that aluminum hexacyanoferrate (II) complexes are partially soluble in various concentrations of ammonium hydroxide with colour changes at boiling temperature, while those of chromium and indium are partially soluble at high concentration of ammonium hydroxide and insoluble at low concentration, respectively at when boiling, those of barium, stannous, vanadium and platinum are insoluble in various concentrations of ammonium hydroxide at boiling temperature.



Table 7: Stability of metal hexacyanoferrate (II) complexes in sulphuric acid at boiling temperature

MFcs (OC)	2.0 M	1.0 M	0.5 M	0.2 M	0.1 M
AlFc (Light blue)	Partially soluble blue turn black				
BaFc (Pale Greenish white)	Insoluble pale green particles turn dark				
CrFc (Bright green)	Partially soluble bright green	Partially soluble bright green	Partially soluble green	Partially soluble green	Partially soluble green
InFc (Light blue)	Partially soluble blue	Partially soluble blue	Partially soluble blue	Partially soluble grey	Partially soluble grey
PtFc (Dark blue)	Insoluble dark blue	Insoluble dark blue	Insoluble blue	Insoluble blue	Insoluble blue
SnFc (Blue)	Partially soluble blue particles turn dark				
VaFc (Dark green)	Insoluble green particles turn black				

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 20 minutes

Volume of acids = 10 mL

Room temperature = 31.0°C

The colour changes of metal hexacyanoferrate (II) complexes in various bases are mainly due to electronic transition within metal hexacyanoferrate (II) complex molecules.

Stability of metal hexacyanoferrate (II) complexes in various concentrations in various solvents at room temperature

It is observed from Table 14 that complexes of aluminum hexacyanoferrate (II) and those of barium, chromium, indium and platinum are insoluble in various organic solvents; (ether, acetone, ethanol, and formaldehyde) at room temperature, those of stannous and vanadium are insoluble in ether, but they are soluble in acetone, ethanol and formaldehyde.

Stability of metal hexacyanoferrate (II) complexes in tap water and sea water at room and boiling temperature

It is clear from Table 15 that metal hexacyanoferrate (II) complexes of aluminum, stannous, chromium, indium, vanadium and platinum are found to be insoluble and stable in tap water and sea water at room and boiling temperature. Barium ferrocyanide is found to be partially soluble in tap water and sea water at room and boiling temperatures.

Effects of visible light on the stability of metal hexacyanoferrate (II) complexes

It is observed from Table 16 that hexacyanoferrate (II) complexes of platinum, stannous and vanadium are stable to visible light until 48 hours of irradiations. It is also observed from Table 16 that those of aluminum, stannous, chromium and indium are unstable in visible light at 12 hours of irradiations.



Table 8: Stability of metal hexacyanoferrate (II) complexes in sodium hydroxide at room temperature

MFcs (OC)	2.0 M	1.0 M	0.5 M	0.2 M	0.1 M
AlFc (Light blue)	Slightly soluble light blue particles change to black	Partially light blue particles change to black	Partially light blue particles change to black	Partially light blue particles change to black	Partially light blue particles change to black
BaFc (Pale greenish white)	Insoluble pale greenish white particles change to black	Insoluble greenish white particles change to black	Insoluble greenish white particles change to black	Insoluble greenish white particles change to black	Insoluble greenish white particles change to black
CrFc (Bright green)	Slightly solubly deep green Particles Change to light green	Slightly solubly dark green	Insoluble dark green particles	Insoluble dark green particles	Insoluble dark green particles
InFc (Light blue)	Slightly soluble Bluish white Particles changed to white	Slightly soluble light blue particles	Insoluble blue particles	Insoluble grey particles	nsoluble grey particles
PtFc (Dark blue)	Insoluble dark blue Particles changed to brown	Insoluble black Particles	Insoluble black Particles	Insoluble brown Particles	Insoluble brown Particles
SnFc (Blue)	Insoluble blue particles changed to brown	Insoluble blue particles changed to brown	Insoluble blue particles changed to yellow	Insoluble blue particles changed to yellow	Insoluble blue particles changed to yellow
VaFc (Dark green)	Insoluble dark green particles changed to black	Insoluble dark green particles changed to black	Insoluble dark green particles changed to black	Insoluble dark green particles changed to black	Insoluble dark green particles changed to black

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 20 minutes

Volume of acids = 10 mL

Room temperature = 31.0°C

Effects of ultraviolet light on the stability of metal hexacyanoferrate (II) complexes

From Table 17 we see that complexes of hexacyanoferrate (II) of stannous, vanadium and platinum are stable to Ultraviolet light until 48 hours of irradiations. Also that those of aluminum, barium, chromium and indium are stable in ultraviolet light at 12 hours of irradiations.

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

Test on oxidizing and photosensitizing activity of metal hexacyanoferrate (II) complexes in potassium iodine and freshly prepared starch solution indicated platinum, chromium and indium hexacyanoferrate (II) complexes as possible oxidizer and photosensitizer during the course of chemical evolution on primitive earth.



Table 9: Stability of metal hexacyanoferrate (II) complexes in sodium hydroxide at boiling temperature

MFcs (OC)	2.0 M	1.0 M	0.5 M	0.2 M	0.1 M
AlFc (Light blue)	Partially soluble blue particles turn black				
BaFc (Pale greenish white)	Partially soluble green particles turn black				
CrFc (Bright green)	Partially soluble light green	Partially soluble light green	Partially soluble dark green	Insoluble dark green	Insoluble dark green
InFc (Light blue)	Partially soluble light blue	Partially soluble light blue	Partially soluble blue	Insoluble grey	Insoluble grey
PtFc (Dark blue)	Insoluble black	Insoluble black	Insoluble brown	Insoluble brown	Insoluble brown
SnFc (Blue)	Insoluble blue particles turn black				
VaFc (Dark green)	Insoluble dark green particles turn black				

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 20 minutes

Volume of acids = 10 mL

Room temperature = 31.0° C

CONCLUDING REMARKS

The following conclusions can be drawn from the present study:

1. The stability of hexacyanoferrate (II) complexes of aluminum, platinum, barium, chromium, stannous and vanadium were found to be affected by heat and light (visible, ultraviolet).
2. Complexes of hexacyanoferrate (II) of barium were found to be insoluble in various concentrations of hydrochloric acid at room temperature and temperature of boiling.
3. Barium, platinum and vanadium ferrocyanides are found to be insoluble in various concentration of sulphuric acid at room temperature and temperature of boiling.
4. Complexes of hexacyanoferrate (II) of barium, stannous, vanadium and platinum were found to be insoluble in various concentrations of potassium hydroxide and ammonium hydroxide at room temperature and temperature of boiling.
5. Chromium, indium, platinum, stannous, aluminum and vanadium ferrocyanides were found to be insoluble and stable in tap water and sea water at room temperature and temperature of boiling.
6. Complexes of hexacyanoferrate (II) of platinum, stannous and vanadium were found to be stable to UV and visible light after 48 hours of irradiations.
7. Chromium, indium and platinum ferrocyanides were found to be possible oxidizer and photosensitizer during the course of chemical evolution on primitive earth.
8. Complexes of hexacyanoferrate (II) of aluminum, barium, chromium, indium and platinum were found to be insoluble in ether, acetone, ethanol and formaldehyde at room temperature.



9. It is also concluded from present study that hexacyanoferrate (II) complexes are insoluble and stable during the course of chemical evolution on primitive earth and played a significant role in condensation of precursors of early life in primeval seas.

Table 10: Stability of metal hexacyanoferrate (II) complexes in potassium hydroxide at room temperature

MFcs (OC)	2.0 M	1.0 M	0.5 M	0.2 M	0.1 M
AlFc (Light blue)	Partially soluble blue particles turn black				
BaFc (Pale greenish white)	Insoluble green particles turn black				
CrFc (Bright green)	Partially soluble bright green	Partially soluble bright green	Insoluble dark green	Insoluble dark green	Insoluble dark green
InFc (Light blue)	Partially soluble light blue	Partially soluble light blue	Insoluble blue	Insoluble grey	Insoluble grey
PtFc (Dark blue)	Insoluble dark blue	Insoluble dark blue	Insoluble black	Insoluble black	Insoluble brown
SnFc (Blue)	Insoluble blue particles turn yellow				
VaFc (Dark green)	Insoluble green particles turn black				

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 20 minutes

Volume of acids = 10 mL

Room temperature = 31.0° C

EXPERIMENTAL

Chemicals

Potassium ferrocyanide, aluminum chloride, barium chloride, sodium vanadate, stannouschloride, chromic chloride, indium chloride, platinum chloride were obtained from BHD Poole, England.

All chemicals used without further purification. Solutions were prepared in doubly distilled water.

Synthesis of metal ferrocyanides

Aluminium, barium, indium and platinum ferrocyanides were prepared by adding metal chlorides (500 mL, 0.1 M) and potassium ferrocyanide (167 mL, 0.1 M) solutions with constant stirring [14].

The reaction mixture was heated on water bath for 3 hours and kept as such at room temperature for 24 hours. The precipitate was filtered under vacuum, washed several times with distilled water and dried in an air oven at 60°C. the driest product was grounded and sieved to 125 µm particles size.



Table 11: Stability of metal hexacyanoferrate (II) complexes in potassium hydroxide at boiling temperature

MFcs (OC)	2.0 M	1.0 M	0.5 M	0.2 M	0.1 M
AlFc (Light blue)	Partially soluble blue particles turn black				
BaFc (Pale greenish white)	Insoluble green particles turn black				
CrFc (Bright green)	Partially soluble bright green	Partially soluble bright green	Partially soluble bright green	Insoluble green	Insoluble green
InFc (Light blue)	Partially soluble light blue	Partially soluble blue	Partially soluble blue	Insoluble grey	Insoluble grey
PtFc (Dark blue)	Insoluble black	Insoluble black	Insoluble brown	Insoluble brown	Insoluble brown
SnFc (Blue)	Insoluble blue particles turn yellow	Insoluble blue particles turn yellow	Insoluble blue particles turn black	Insoluble blue particles turn black	Insoluble blue particles turn black
VaFc (Dark green)	Insoluble green particles turn black				

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 20 minutes

Volume of acids = 10 mL

Room temperature = 31.0° C

Stannous ferrocyanide was prepared by mixing solutions of 0.25 M potassium ferrocyanide and stannous chloride in the ratio (2:1) with constant stirring [15]. The precipitate was cured at room temperature for 24 hours. The precipitate was filtered under vacuum, washed several times with distilled water and was dried in an air oven at 60°C. The driest product was grounded and sieved to 125 µm particles size.

Vanadium ferrocyanide complex was isolated by adding (10 mL, 1.0 M) HCl to mixture containing sodium vanadate (500 mL, 0.1 M) and potassium ferrocyanide (500 mL : 0.1 M) solution stirred constantly [16]. Reaction mixture to be heated on boiling water bath for 3.5 hours then allowed to cool at room temperature overnight. The precipitate formed was filtered and dried at 60°C in an air oven. The driest product was grounded and sieved to 125 µm particles size.

Chromium ferrocyanide was prepared under optimum experimental conditions according to the procedure of Malik et al. [17].

Characterization of metal ferrocyanides

Aluminium, barium, chromium, indium, platinum, stannous and vanadium ferrocyanides are light blue, pale greenish white, bright green, light blue, dark blue, blue and dark green colours, respectively. These metal hexacyanoferrate (II) complexes are amorphous insoluble solid and showed no X-ray pattern. The metal hexacyanoferrate (II) complexes were characterized on the basis of elemental analysis and spectral studies. The percentage compositions of metals were determined by IL-751 atomic absorption spectrophotometer [18]. Carbon hydrogen and nitrogen analysis were carried out by CEST-18, CHN analyzer (Table 1).

Infrared spectra of metal hexacyanoferrate (II) complexes were recorded in KBr disc on Beckman IR-20 spectrophotometer. All seven metal hexacyanoferrate (II) complexes show a broad peak at 3040-3700 cm⁻¹ is characteristic of water molecule and OH groups. A peak at around 1510-1660 cm⁻¹ is due to HOH bending [19], two



sharp peaks, one at around 2000 cm^{-1} and the other at around 600 cm^{-1} in all seven spectra of complexes are characteristics frequencies of cyanide and Fe-C stretching, respectively [20].

Another sharp band at $489\text{-}500\text{ cm}^{-1}$ in all seven metal hexacyanoferrate (II) complexes probably shows the presence of metal-nitrogen bond thus indicating a certain degree of polymerization in the products [21, 22] (Table 2).

Table 12: Stability of metal hexacyanoferrate (II) complexes in ammonium hydroxide at room temperature

MFcs (OC)	2.0 M	1.0 M	0.5 M	0.2 M	0.1 M
AlFc (Light blue)	Partially soluble blue particles turn black				
BaFc (Pale greenish white)	Insoluble green particles turn black				
CrFc (Bright green)	Partially soluble dark green	Partially soluble dark green	Insoluble dark green	Insoluble green	Insoluble green
InFc (Light blue)	Partially soluble light blue	Partially soluble light blue	Insoluble blue	Insoluble blue	Insoluble grey
PtFc (Dark blue)	Insoluble black	Insoluble black	Insoluble black	Insoluble brown	Insoluble brown
SnFc (Blue)	Insoluble blue particles turn yellow	Insoluble blue particles turn yellow	Insoluble blue particles turn black	Insoluble blue particles turn black	Insoluble blue particles turn black
VaFc (Dark green)	Insoluble green particles turn black				

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 20 minutes

Volume of acids = 10 mL

Room temperature = 31.0°C

Stability study on metal ferrocyanides

Effect of heat on the stability of metal hexacyanoferrate (II) complexes

A20 mg of each metal hexacyanoferrate (II) complexes was placed in a petri dishes. Petri dishes were dried in the air oven for 6 hours at 100°C . This process was repeated at 150°C , 200°C , 250°C to demonstrate the effect of heat on the various metal hexacyanoferrate (II) complexes. The colour of metal hexacyanoferrate (II) complexes at various temperatures was observed. The effect of heat on the stability of metal hexacyanoferrate (II) complexes is shown in Table 3.

Stability of metal hexacyanoferrate (II) complexes in various concentrations of acids at room temperature and at boiling temperature

The metal hexacyanoferrate (II) complexes (20 mg) were placed in the test tubes containing 10 mL of each 2.0 M, 1.0 M, 0.5 M, 0.2 M and 0.1 M acids (HCl , H_2SO_4). The mixture was agitated for 20 minutes at room temperature and observation for any change in colour of metal hexacyanoferrate (II) complexes were recorded (Tables 4, 6). The same reaction mixture boiled on a Bunsen flame for 20 minutes and any change in colour of metal hexacyanoferrate (II) complexes were recorded (Tables 5, 7). This process was repeated for each metal hexacyanoferrate (II) complexes. The colour change for metal hexacyanoferrate (II) complexes was recorded.



Stability of metal hexacyanoferrate (II) complexes in various concentrations of bases at room temperature and at boiling temperature

Metal hexacyanoferrate (II) complexes (20 mg) were placed in the test tubes containing 10 mL of 2.0 M, 1.0 M, 0.5 M, 0.2 M and 0.1 M bases (NaOH , KOH, NH₄OH).The mixture was agitated for 20 minutes at room temperature and observation for any change in colour of metal hexacyanoferrate (II) complexes were recorded (Tables 8, 10, 12). The same reaction mixture boiled on a Bunsen flame for 20 minutes and any change in colour of metal hexacyanoferrate (II) complexes were recorded (Tables 9, 11, 13). This process was repeated for each metal hexacyanoferrate (II) complexes. The colour change for metal hexacyanoferrate (II) complexes was recorded.

Stability of metal hexacyanoferrate (II) complexes in various organic solvents at room temperature

Metal hexacyanoferrate (II) complexes (20 mg) were placed in test tubes containing 10 mL each of ether, acetone, ethanol, formaldehyde. The mixture was agitated for 20 minutes and kept at room temperature for 1 hour then any change in colour of metal hexacyanoferrate (II) complexes were recorded (Table 14).

Table 13: *Stability of metal hexacyanoferrate (II) complexes in ammonium hydroxide at boiling temperature*

MFcs (OC)	2.0 M	1.0 M	0.5 M	0.2 M	0.1 M
AlFc (Light blue)	Partially soluble blue particles turn black				
BaFc (Pale Greenish white)	Insoluble green particles turn black				
CrFc (Bright green)	Partially soluble bright green	Partially soluble bright green	Partially soluble dark green	Insoluble green	Insoluble green
InFc (Light blue)	Partially soluble blue	Partially soluble blue	Partially soluble blue	Insoluble grey	Insoluble grey
PtFc (Dark blue)	Insoluble dark blue	Insoluble dark blue	Insoluble black	Insoluble brown	Insoluble brown
SnFc (Blue)	Insoluble blue particles turn black				
VaFc (Dark green)	Insoluble green particles turn black				

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.
 Time: 20 minutes

Volume of acids = 10 mL
 Room temperature = 31.0° C

Stability of metal hexacyanoferrate (II) complexes in tap water and sea water at room temperature and at boiling temperature

The metal hexacyanoferrate (II) complexes (20 mg) were placed in the test tubes containing tapwater and sea water. The mixture was agitated for 20 minutes and observation for any change in colour of metal hexacyanoferrate (II) complexes were recorded (Table 15). The same reaction mixture boiled on Bunsen flame for 20 minutes and any change in colour of metal hexacyanoferrate (II) complexes were recorded (Table 15).



Effect of light (UV/Vis) on the stability of metal hexacyanoferrate (II) complexes

A 20 mg of each metal hexacyanoferrate (II) complexes were placed in a dry petri dish and the original colour was recorded. A 250W visible lamp was kept vertically above the sample at a distance of 28 cm. The observations for any change in colour of metal hexacyanoferrate (II) complexes were recorded at 12, 24, 36 and 48 hours (Table 16). The same experiment was repeated using a long wave (300 – 380 nm) UV lamp. The observations of any change in colour of metal hexacyanoferrate (II) complexes were recorded (Table 17).

Table 14: Stability of metal hexacyanoferrate (II) complexes in various organic solvents at room temperature

MFcs (OC)	Ether	Acetone	Ethanol	Formaldehyde
AlFc (Light blue)	Insoluble light blue particles changed to blue green	Insoluble light blue particles changed to blue green	Insoluble light blue particles changed to blue green	Insoluble light blue particles changed to blue green
BaFc (Pale greenish white)	Insoluble pale greenish white particles changed to off-white	Insoluble pale greenish white particles changed to light green	Insoluble pale greenish white particles changed to light green	Insoluble pale greenish white particles changed to light green
CrFc (Bright green)	Insoluble no colour change	Insoluble no colour change	Insoluble no colour change	Insoluble no colour change
InFc (Light blue)	Insoluble white particles	Insoluble white particles	Insoluble colour change from bluish white to white	Insoluble white particles
PtFc (Dark blue)	Insoluble no colour Change	Insoluble no colour change	Insoluble no colour change	Insoluble no colour change
SnFc (Blue)	Insoluble dark particles changed to dark blue	Soluble dark blue	Soluble dark blue	Soluble dark blue
VaFc (Dark green)	Insoluble dark blue	Soluble dark green	Soluble brown	Soluble black

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 20 minutes

Volume of organic solvents = 10 mL

Room temperature = 31.0° C

Test on oxidizing and photosensitizing activity of metal ferrocyanides

The oxidizing and photosensitizing potential of metal ferrocyanides were compared by potassium iodide and freshly prepared 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 0.1M potassium iodide solution. A 25 mg of hexacyanoferrate (II) complexes were added into each test tube and agitated, observation for any decolorization of blue color and potassium iodide and starch solution were recorded. The same experiment was repeated using a 250W visible lamp and a long wave UV lamp, which was kept vertically above the test tubes at a distance of 15.0 cm. Photosensitizer will decolorize the blue color of potassium



iodide and starch solution in the presence of visible and ultraviolet light. The oxidizers will decolorize the blue color of potassium iodide and starch solution in the absence of light.

Table 15: Stability of metal hexacyanoferrate (II) complexes in sea water and tap water (at boiling temperature and at room temperature)

MFcs (OC)	Tap water		Sea water	
	Room Temperature	Boiling temperature	Room temperature	Boiling temperature
AlFc (light blue)	Insoluble light blue particles did not change			
BaFc (Pale greenish White)	Partially soluble	Partially soluble	Partially soluble	Partially soluble
CrFc (Bright green)	Insoluble bright green particles did not change			
InFc (Light blue)	Insoluble light blue particles did not change			
PtFc (Dark blue)	Insoluble dark blue particles did not change			
SnFc (Blue)	Insoluble blue particles did not change			
VFc (Dark green)	Insoluble dark green Particles did not change			

OC = Original colour of metal ferrocyanides

Amount of metal ferrocyanides = 20 mg.

Time: 20 minutes

Volume of organic solvents = 10 mL

Room temperature = 31.0° C

Table 16: Effects of light (Visible) on the stability of metal hexacyanoferrate (II) complexes

MFcs	Original colour	12 hrs	24 hrs	36 hrs	48 hrs
AlFc	Light blue	Light yellow	Light yellow	Light yellow	Light yellow
BaFc	Pale greenish white	Greenish white	Greenish white	Greenish white	Greenish white
CrFc	Bright green	Light green	Light green	Light green	Light green
InFc	Light blue	Light yellow	Light yellow	Light yellow	Light yellow
PtFc	Dark blue	Dark blue	Dark blue	Dark blue	Dark blue
SnFc	Blue	Blue	Blue	Blue	Blue
VaFc	Dark green	Dark green	Dark green	Dark green	Dark green

Amount of metal ferrocyanides = 20 mg.

Lamp = 250 Watts, VIS

Distance of lamp from the metal ferrocyanides = 28 cm



Table 17: Effects of light (Ultra-violet) on the stability of metal hexacyanoferrate (II) complexes

MFcs	Original colour	12 hrs	24 hrs	36 hrs	48 hrs
AlFc	Light blue	Light yellow	Light yellow	Light yellow	Light yellow
BaFc	Pale greenish white	Greenish white	Greenish white	Greenish white	Greenish white
CrFc	Bright green	Light green	Light green	Light green	Light green
InFc	Light blue	Yellow	Yellow	Yellow	Yellow
PtFc	Dark blue	Dark blue	Dark blue	Dark blue	Dark blue
SnFc	Blue	Blue	Blue	Blue	Blue
VaFc	Dark green	Dark green	Dark green	Dark green	Dark green

Amount of metal ferrocynides = 20 mg.

Lamp = 220 Watts, UV, long wave (380 nm)

Distance of lamp from metal ferrocynides = 28 cm

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