

Interaction of Aromatic Amino Acids with Metal Hexacyanochromate(III) Complexes: A Possible Role in Chemical Evolution

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Metal cyanogen complexes have been proposed to be efficient prebiotic catalysts. Insoluble metal cyanogen complexes are thought to have concentrated biomonomers from dilute prebiotic soup which facilitated a class of prebiotic reactions. Thus, large biopolymers were able to form during the course of chemical evolution and the origin of life. Based on this hypothesis, the interaction of two naturally occurring α-aromatic amino acids, tryptophan and phenylalanine, with cobalt(II), copper(II), and cadmium(II) hexacyanochromate(III) has been studied, and the interaction was found to be strongest at neutral pH ($\approx$7.0). Cobalt(II) hexacyanochromate(III) adsorbed the largest amount of both amino acids while tryptophan had a stronger affinity than phenylalanine. Infrared spectral studies of the metal hexacyanochromate(III) complexes, amino acids and metal hexacyanochromate(III)–amino acid adducts indicated the involvement of NH_2 as well as COO^- groups of amino acids and surface metal ions present in the lattice of the metal hexacyanochromate(III) complexes.

Besides their potential applications as adsorbents, ion exchangers, molecular sieves, catalysts, and pigments, metal cyanogen complexes have been proposed to play an important role in prebiotic synthesis, which is a matter of active research among the scientists from different disciplines. From the middle of the last century, a vast number of workers have focused their attention on tracing out the various steps involved in chemical evolution and the origin of life on Earth.

It is assumed that some of the important biomonomers, such as amino acids, purine and pyrimidine nitrogen bases, nucleotides, pentose sugars, etc., were synthesised in a prebiotic environment[1] and subsequently polymerized into large biopolymers during the course of chemical evolution and origin of life. Since it is unlikely that the prebiotic synthesis of biomonomers would have yielded high concentrations of these biomolecules in primeval seas, the mechanisms and the reagents through which biomonomers were concentrated from their dilute aqueous solutions and polymerized into large biopolymers have received growing interest. Adsorptive interaction processes and the solid surfaces of inorganic minerals, respectively, have been proposed to play important roles in concentrating the biomonomers from a dilute prebiotic soup.[2–4] The adsorptive interaction processes could have brought the organic molecules closer to each other which would accelerate the kinetics of a series of prebiotic chemical reactions.

Cyanide has been reported as a product in some of the simulated prebiotic experiments and is thought to have been readily available in prebiotic environments. Use of cyano compounds as precursors for biological compounds, including amino acids, purine and pyrimidines has been reviewed by Ferris and Hagan.[5] Synthesis of 2,3′-cAMP starting from cyano-derived compounds has also been demonstrated by Ferris et al.[6] Since cyanide ions are negatively charged, good σ donors and good π acceptors, act as strong field ligands and easily coordinate to transition-metal ions, it is, therefore, reasonable to assume that cyanide ions might have complexed with transition-metal ions present in primeval seas forming a number of soluble and insoluble metal cyanogen complexes. As most of the metal cyanogen complexes are insoluble in water, they may have locally settled at the bottom of primeval sea or on its shore. It is proposed that biomonomers present in the prebiotic soup might have interacted on the solid surfaces of metal cyanogen complexes, and thus, they were concentrated from dilute aqueous solutions in primeval seas. The biomonomers would have been protected from degradation and undergone a class of reactions, such as condensation, dimerisation, oligomerisation, redox reactions, etc., to afford the essential materials needed to form the first living cell. In view of this hypothesis, the interaction of organic molecules, including amino acids, nucleotides, amino pyridines, and aromatic amines, with different metal cyanogen complexes have been studied, and the results suggest that they have active role in chemical evolution.[7–16] In this paper, we report the results of our study on the interaction of tryptophan and phenylalanine with cobalt(II), copper(II), and cadmium(II) hexacyanochromate(III) exploring their possible role in chemical evolution. Existence of aromatic amino acids on primitive Earth has been proposed by Friedmann and Miller.[17]

Experimental

Chemicals. Potassium dichromate (B.D.H.), acetic acid (E. Merck), potassium cyanide (Loba Chemie), cobalt(II) nitrate (E. Merck), copper(II) nitrate (E. Merck), cadmium(II) nitrate (E. Merck), tryptophan (E. Merck), and phenylalanine (E. Merck) were used as received. All other chemicals were of analytical reagent grade.

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Preparation of Metal Hexacyanochromates(III). All three metal hexacyanochromates(III) were synthesized from potassium hexacyanochromate(III), which was synthesized using Christensen's method.[18] To synthesize potassium hexacyanochromate(III), 25 grams of potassium dichromate was dissolved in 500 mL of water, and SO_2 gas was passed through the solution to reduce Cr^{6+} to Cr^{3+}. This solution was then boiled to remove the excess SO_2. To the above boiling solution, liquid ammonia was added slowly with vigorous stirring to precipitate chromium(III) hydroxide. The chromium(III) hydroxide was collected by filteration, washed with hot water, and then, kept in a casserole in order to prevent its conversion to insoluble chromium(III) oxide through the loss of water molecules. The wet chromium(III) hydroxide was dissolved in 100 mL of glacial acetic acid, and this solution was evaporated to near dryness and was taken up with 180 mL of water. It was then poured into a flask containing a boiling solution of 75 grams of potassium cyanide in 300 mL of water. The reaction mixture was cooled, filtered, concentrated to 300 mL and filtered again while still hot. On cooling the solution, pale-yellow needles of potassium hexacyanochromate(III) formed, were collected and washed with a little cold water. Finally, it was recrystallized from water at ca. 5 °C.

Cobalt(II), copper(II), and cadmium(II) hexacyanochromate(III) were prepared using the double decomposition method. 167 mL of a 0.1 M solution of potassium hexacyanochromate(III) was added to 500 mL of a 0.1 M solution of cobalt(II) nitrate or copper(II) nitrate or cadmium(II) nitrate, respectively, with constant stirring. The excess metal salts were used to improve the coagulation of precipitate. The reaction mixtures were kept as such for 24 h. The precipitate was collected by filteration, washed thoroughly with water and dried. The dried products were ground and sieved to 100-mesh size. CHN analyses, X-ray diffraction, thermogravimetric analyses, differential thermal analyses and infrared spectral studies of all three metal hexacyanochromates(III) were performed in order to test the purity of the complexes.

Elemental Analyses. The percentage of carbon, nitrogen, and hydrogen in all the three metal hexacyanochromate(III) was determined with an Elementar Vario ELHI CHN analyzer. The percent composition of the metals in the complexes was determined using a Perkin-Elmer 3100 Atomic Absorption Spectrophotometer. The data are summarized in Table 1.

Thermogravimetric and Differential Thermal Analyses. Thermogravimetric analysis of all three metal hexacyanochromate(III) was carried out using a Perkin-Elmer Thermogravimetric Analyzer (Model:Pyris Diamond). The heating rate was 10 $^{\circ}C\,min^{-1}$. All measurements were carried out in a static air atmosphere using Al_2O_3 as a reference. The thermogravimetric and differential thermal spectra showed a mass loss corresponding to 14, 6, and 14 water molecules in cobalt(II), copper(II), and cadmium(II) hexacyanochromate(III), respectively.

X-ray Diffraction Studies. The X-ray diffraction analyses of all three powdered metal hexacyanochromate(III) complexes was carried out using a Philips PW-1140/90 X-ray diffractometer. The relative-intensity data and interplaner spacing (d) values were in good agreement with the reported values,[19] Table 2.

Spectral Studies. Electronic spectra of tryptophan and phen-

Table 1. Elemental Analysis of the Metal Hexacyanochromate(III) Complexes[a)]

Metal hexacyanochromate(III)	C%	N%	H%	M%	M′%[b)]
Cobalt(II) hexacyanochromate(III)	16.78	18.43	3.44	21.00	12.56
	(17.04)	(18.88)	(3.31)	(20.95)	(12.31)
Copper(II) hexacyanochromate(III)	16.51	18.79	2.22	26.13	13.00
	(16.89)	(19.01)	(1.98)	(26.67)	(13.56)
Cadmium(II) hexacyanochromate(III)	13.95	15.83	2.76	34.13	10.44
	(14.34)	(16.11)	(2.79)	(33.47)	(10.36)

a) Bracket values represent the theoretical values. b) M′ is exchangeable transition metal.

Table 2. X-ray Diffraction Data for the Metal Hexacyanochromate(III) Complexes[a)]

Cobalt(II) hexacyanochromate(III)		Copper(II) hexacyanochromate(III)		Cadmium(II) hexacyanochromate(III)	
d/Å	I/I^o	d/Å	I/I^o	d/Å	I/I^o
5.16	78	5.14	100	6.24	61
(5.18)	(80)	(5.14)	(100)	(6.22)	(60)
3.67	100	3.65	97	5.41	100
(3.66)	(100)	(3.66)	(100)	(5.47)	(100)
2.59	82	3.15	11	3.83	98
(2.59)	(80)	(3.14)	(10)	(3.88)	(100)
2.32	61	2.56	83	3.28	59
(2.31)	(60)	(2.58)	(80)	(3.30)	(60)
		2.34	61	2.73	82
		(2.33)	(60)	(2.73)	(80)
				2.44	81
				(2.44)	(80)
				2.23	48
				(2.24)	(50)

a) Bracket values represent the reported values.

ylalanine were recorded on a Beckman DU-6 Spectrophotometer. The characteristic values of λ_{max} for tryptophan and phenylalanine were observed as 278 and 258 nm, respectively. Infrared spectra of the amino acids, metal hexacyanochromate(III) complexes and amino acid–metal hexacyanochromate(III) adducts were recorded as KBr discs on a Perkin-Elmer F.T.I.R. Spetrophotometer.

Adsorption Studies. Adsorption of tryptophan and phenylalanine on all three metal hexacyanochromate(III) complexes was studied by adding 10 mL aliquots of amino acids solutions to 50 mg metal hexacyanochromate(III) complex. The pH was adjusted by adding small volumes of concentrated solutions of HCl or NaOH depending on the pH. The suspensions were shaken using an Expo Shaker initially for 1 h and then allowed to equilibrate at 25 °C with intermittent shaking. The suspensions were centrifuged after 24 h and the supernatant liquid was decanted. The amino acid concentration was determined spectrophotometrically. The amount of the amino acids adsorbed was calculated from the difference between the concentrations before and after adsorption. The equilibrium concentration of amino acids and their amount adsorbed were used to obtained adsorption isotherms. The pH of the supernatant liquids was recorded with a pH meter (model CP-90, manufactured by Toshniwal Instruments Manufacturer Pvt. Ltd., Ajmer).

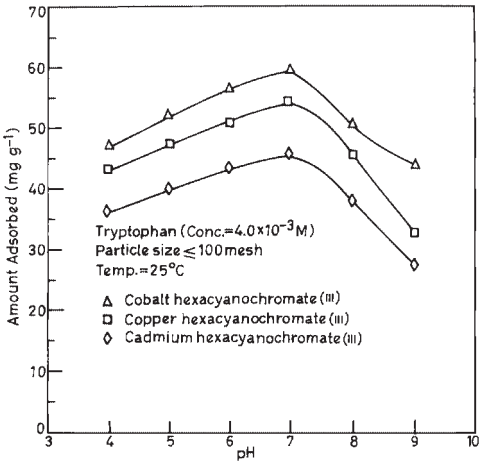
Results

CHN analyses, atomic absorption spectrophotometric studies, thermogravimetric and differential thermal analyses was used to verify that the structural formulae of the synthesized complexes was similar to the reported formulae, i.e., $Co_3[Cr(CN)_6]_2 \cdot 14H_2O$, $Cu_3[Cr(CN)_6]_2 \cdot 6H_2O$, and $Cd_3[Cr(CN)_6]_2 \cdot 14H_2O$. Further, X-ray diffraction studies confirmed the purity of the synthesized complexes as there was no significant difference in the observed and reported relative-intensity and interplanar spacing (d) values[19] as shown in Table 2.

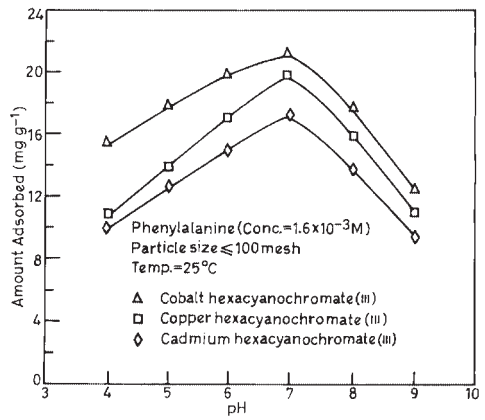
The effect of pH on the interaction of amino acids with all three metal hexacyanochromate(III) complexes was studied over a wide pH range (5.0–9.0). 10 mL of the amino acid solutions with fixed concentrations (4.0×10^{-3} M for tryptophan and 1.60×10^{-3} M for phenylalanine) were used to study their adsorption onto all three metal hexacyanochromate(III) complexes as a function of pH. The change in the amount of amino acids adsorbed on different metal hexacyanochromate(III) complexes and at different pH values are shown in Figs. 1a and 1b. Results indicate a maximum adsorption at neutral pH and less adsorption under acidic as well as basic conditions in each case. Tryptophan showed more adsorption than phenylalanine towards all three metal hexacyanochromate(III) complexes. Adsorption data obtained at a neutral pH and wide concentration range of amino acids (0.5×10^{-3}–4.0×10^{-3} M in case of tryptophan, 2.0×10^{-4}–1.6×10^{-3} M in case of phenylalanine) were fitted as Langmuir Adsorption Isotherms as shown in Figs. 2a and 2b. The isotherms indicate that the adsorption is fast, regular, positive and concave to the concentration for both amino acids studied. The adsorption data followed the equation:

$$C_{eq}/X_e = 1/K_L X_m + C_{eq}/X_m, \quad (1)$$

where C_{eq} is equilibrium concentration of the amino acids; K_L is a constant related to enthalpy (ΔH) of the adsorption



(a)



(b)

Fig. 1. (a) Adsorption of tryptophan (4.0×10^{-3} M) on metal hexacyanochromates(III) with a particle size less than 100 mesh at room temperature as a function of pH. (b) Adsorption of phenylalanine (1.6×10^{-3} M) on metal hexacyanochromates(III) with a particle size less than 100 mesh at room temperature as a function of pH.

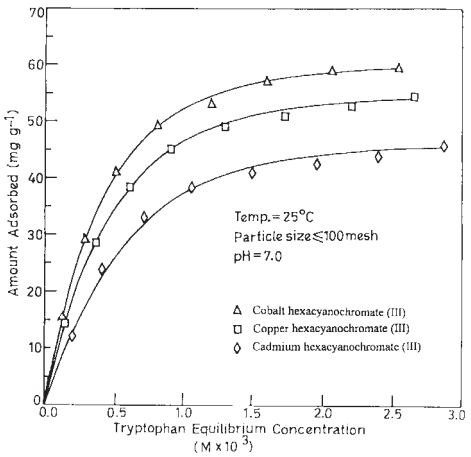
($K_L \alpha e^{-\Delta H/RT}$), X_e is the amount (mg) of amino acid adsorbed per gram weight of metal hexacyanochromate(III) and X_m is the amount (mg) of the amino acid required per gram weight of the metal hexacyanochromate(III) complexes for a complete monolayer to form. The K_L and X_m values were determined and are shown in Table 3. The percent binding of tryptophan and phenylalanine is listed in Table 4. The values of X_m and percent binding data means that the interaction with tryptophan is greater than phenylalanine towards all three metal hexacyanochromate(III) complexes. Cobalt(II) hexacyanochromate(III) showed the maximum uptake capacity among the three metal hexacyanochromate(III) complexes studied. The order of uptake capacity was found as follow:

Cobalt(II) hexacyanochromate(III)
> Copper(II) hexacyanochromate(III)
> Cadmium(II) hexacyanochromate(III) (2)

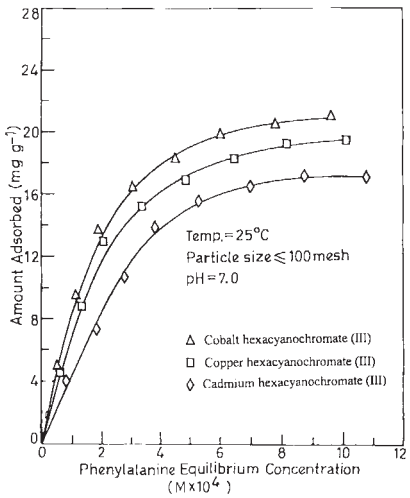
The infrared spectra of metal hexacyanochromate(III) complexes, amino acids, and metal hexacyanochromate(III)–amino

Table 3. Langmuir Constants for Adsorption of Aromatic Amino Acids on the Metal Hexacyanochromate(III) Complexes

Metal hexacyanochromate(III)	Tryptophan		Phenylalanine	
	K_L/dm^3 mol^{-1}	X_m/mg g^{-1}	K_L/dm^3 mol^{-1}	X_m/mg g^{-1}
Cobalt(II) hexacyanochromate(III)	2.67	69.44	0.57	25.25
Copper(II) hexacyanochromate(III)	2.21	64.52	0.48	24.98
Cadmium(II) hexacyanochromate(III)	1.87	54.65	0.28	23.92



(a)



(b)

Fig. 2. (a) Adsorption of tryptophan on metal hexacyanochromates(III) with a particle size less than 100 mesh at neutral pH and room temperature. (b) Adsorption of phenylalanine on metal hexacyanochromates(III) with a particle size less than 100 mesh at neutral pH and room temperature.

acid adducts were recorded and analysed. Metal hexacyanochromate(III)–amino acid adducts were washed thoroughly with water, dried and then study by using IR spectroscopy. A pronounced change was observed in the characteristic frequencies of both the amino acids after and before the interaction with the metal hexacyanochromate(III) complexes. Typical frequencies of amino acids corresponding to $\nu_{(NH_2)}$ and $\nu_{(assymCOOH)}$ increase due to the interaction with all three metal hexacyanochromate(III) complexes. Minor changes were observed in the infrared frequencies corresponding to $\nu_{(symCOOH)}$. The results are shown in Table 5. Negligible changes were observed in characteristic frequencies of the metal hexacyanochromate(III) complexes (ν_{Cr-C} and ν_{C-N}) after interaction with both the amino acids.

Table 4. Percent Binding of Aromatic Amino Acids on the Metal Hexacyanochromate(III) Complexes

Metal hexacyanochromate(III)	Percent binding	
	Tryptophan	Phenylalanine
Cobalt(II) hexacyanochromate(III)	41.7	36.2
Copper(II) hexacyanochromate(III)	38.6	32.9
Cadmium(II) hexacyanochromate(III)	33.0	27.0

Discussion

Due to their solid surfaces, various clay minerals have been proposed to play important role in concentrating the biomolecules from dilute prebiotic soup in the primeval seas during the course of chemical evolution. Interaction with a wide variety of organic molecules including amino acids, peptides, nucleic acids and sugars with clays and clay minerals have been studied suggesting their possible role in chemical evolution.[2–5] Since most of the metal cyanogen complexes have solid surfaces that are microporous[20] in nature, they might have interacted with biomolecules in such a way as to concentrate them from dilute aqueous solutions in primeval seas.

The molecular formula of the metal hexacyanochromate(III) complexes has been reported as $M_3[Cr(CN)_6]_2 \cdot nH_2O$, where M represents an exchangeable divalent transition-metal ion and n represents the number of water molecules present in the interstitial site of the lattice. The structure of hexacyanochromate(III) complexes of divalent transition metals is analogous to that of Prussian blue. Shriver[21] has studied the systematics of the lattice parameters for the Prussian blue analogues. The face-centered cubic lattice structure of Prussian blue is the characteristic of many other metal hexacyanometalate. Ferrari et al.[19] reported that the three metal hexacyanochromate(III) complexes have cubic symmetry. The lattice parameters for the cobalt(II), copper(II), and cadmium(II) hexacyanochromate complexes have been reported[19] as 10.36, 10.32, and 10.95 Å, respectively. The transition-metal hexacyanochro-

Table 5. Typical Infrared Spectral Frequencies (cm^{-1}) of Tryptophan and Phenylalanine before and after Adsorption on the Metal Hexacyanochromate(III) Complexes[a)]

Metal hexacyanochromate(III)	Characteristic frequencies/cm^{-1}					
	Phenylalanine			Tryptophan		
	ν_{N-H}	$\nu_{as(COO^-)}$	$\nu_{s(COO^-)}$	ν_{N-H}	$\nu_{as(COO^-)}$	$\nu_{s(COO^-)}$
Cobalt(II)	3390	1596	1404	3409	1590	1408
hexacyanochromate(III)	(3400)	(1608)	(1400)	(3441)	(1606)	(1395)
Copper(II)	3390	1596	1404	3409	1590	1408
hexacyanochromate(III)	(3404)	(1606)	(1398)	(3441)	(1609)	(1392)
Cadmium(II)	3390	1596	1404	3409	1590	1408
hexacyanochromate(III)	(3399)	(1602)	(1400)	(3430)	(1601)	(1392)

a) Bracket values represent frequencies after adsorption.

mate(III) complexes generally have a polymeric lattice structure with $[Cr(CN)_6]^{3-}$ anions, in which the other transition-metal ions are coordinated by the nitrogen atom of the cyanido ligand. Detailed structural studies of the metal hexacyanochromate(III) complexes with the general formula $M_3[Cr(CN)_6]_2 \cdot nH_2O$ were carried out by Ludi and Gudel.[22] Attempts are being made to determine the structures of other metal cyanogen complexes. Recently, Gómez and Reguera reported the structure of cadmium hexacyanoferrate(II).[23]

At lower pH, the lower adsorption of amino acids on the metal hexacyanochromate(III) complexes may be due to the protonation of the amino acid molecules. In alkaline medium, lower adsorption may be due to the interaction between OH^- and the metal hexacyanochromate(III) complexes. The greater adsorption of tryptophan than phenylalanine by all three metal hexacyanochromate(III) complexes may be due to additional interaction through the tryptophan indole ring. The indole ring of tryptophan may interact with surface metal ions present in the lattice of complexes through the donation of π electrons present in the $d\pi$ orbitals of the outer metal ion to the antibonding molecular orbitals of indole ring. The greater adsorption of tryptophan than phenylalanine is consistent with our previous studies.[8] The effect of pH on the amount of amino acids adsorbed could not only be because of the change in the ionic form of amino acids but also due to the change in surface characteristics of the metal hexacyanochromate(III) complexes. The surface conditions of the metal hexacyanochromate(III) complexes due to pH seem to affect the amount of amino acids adsorbed more than the ionic forms of amino acids. It is likely because both amino acids, i.e., tryptophan and phenylalanine, exist as zwitterions over a wide pH range with respect to their isoelectric pH. For intance, the pK_a values for tryptophan are 2.20 and 9.55, so that at pH 4.20 and 7.55, approximately 99% of the tryptophan exists as a zwitterion.

Since no significant change was observed in the IR spectra of the metal hexacyanochromate(III) complexes before and after adsorption, the amino acid molecules do not appear to enter into the inner sphere of the metal hexacyanochromate(III) complexes by replacing CN^- ligands. Moreover, the replacement of CN^- ligands by other ligands is highly improbable.[24] Thus, it is suggested that the amino acid molecules are adsorbed onto the metal hexacyanochromate(III) complexes through interaction between the metal ions of the corresponding metal hexacyanochromate(III) complexes and COO^- as well as NH_2 groups of amino acid molecules.

Conclusion

The results of the present study reveal that insoluble metal hexacyanochromate(III) complexes present at the bottom of shores of primeval seas could have interacted with aromatic amino acids in such a way as to concentrate them from the dilute prebiotic soup during the course of chemical evolution and the origin of life. Biomonomers, thus concentrated, are thought to have been protected from degradation and undergone a class of reactions of prebiotic relevance producing biopolymers essential for the formation of first living cell on this planet.

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