

The Interaction of Ribonucleotides with Metal Hexacyanochromates(III) and the Relevance to Chemical Evolution

Shah Raj Ali and Kamaluddin*

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India

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The interaction of ribonucleotides, namely 5′-AMP, 5′-GMP, 5′-CMP, and 5′-UMP, with cobalt(II) and cadmium(II) hexacyanochromates(III) has been studied. Maximum adsorption was observed at a neutral pH. Adsorption isotherms were found to be Langmuirian in nature. Values for X_m and K_L were calculated. Purine nucleotides showed more adsorption than pyrimidine nucleotides on both the metal hexacyanochromates(III), whereas cobalt(II) hexacyanochromate(III) was found to be a better adsorbent for all of the ribonucleotides studied. Infrared spectral studies of the adsorption adducts suggested that adsorption occurs due to interactions between the phosphate moiety and base residue of the ribonucleotide molecule with outer divalent metal ions present in the lattice of metal hexacyanochromates(III). The results of the present study support the hypothesis that metal cyanogen complexes might play an important role in concentrating and stabilizing the biomonomers on their surfaces through adsorption processes during the course of chemical evolution.

It is now widely accepted that a crucial step in the chemical evolution on the earth involved the polymerization of important biomonomers such as amino acids, nucleotides and pentose sugars that formed from simple molecules in a prebiotic environment.[1] Until now it has not been established how the biomonomers might have concentrated from their dilute aqueous solutions in primeval seas. However, one of the suggestions is that the clays and other minerals might have provided surfaces onto which small molecules could have concentrated.[2–11] Biomonomers thus concentrated would have been protected from degradation and might have undergone reactions such as condensation, oligomerization, and/or redox reactions producing polymeric materials from which life has emerged from a prebiotic environment.[12–15]

The existence of a strong correlation between the concentration of minor transition elements and their biological behavior in primeval seas has been proposed.[16] It indicates the presence of important bio-transition metals such as iron, zinc, manganese, copper, cobalt, etc., in the primeval seas. It is generally accepted that the transition metal ions abundantly present in primeval seas might have complexed with simple molecules available to them.[17] It has been reported that cyanide ions were readily formed in the prebiotic environment.[18] Cyanide ion, being a negatively charged good σ donor and good π acceptor, acts as a strong field ligand and shows greater ease of coordination with transition metal ions with greater crystal field splitting. It is, therefore, reasonable to assume that cyanide ions might have formed a number of soluble and insoluble cyano complexes with the transition metal ions abundantly present in primeval seas. The existence of ferri-ferrocyanides in the Anoxic Archean Hydrosphere has been proposed.[19] Since most of the metal cyanogen complexes are water insoluble, it is assumed that they might have locally settled at the bottom of sea or at the sea shore. We propose that these metal cyanogen complexes might have concentrated the biomonomers on their surfaces through adsorption processes and subsequently catalyzed a class of reactions of prebiotic relevance. The biomonomers thus concentrated might have been protected from degradation and condensed into biopolymers, which might have been essential for prebiotic synthesis.

In order to establish the metal cyanogen complexes as prebiotic catalysts, a number of metal hexacyanoferrates(II) have been synthesized in our laboratory, and their interactions with biomonomers such as amino acids, nitrogen bases and nucleotides have been studied regarding their possible role in chemical evolution on prebiotic earth.[20–24] During these studies, metal hexacyanoferrates(II) have been found to have a high adsorption affinity possessing considerable specific surface area values. They have also been found to be efficient in catalyzing certain reactions of prebiotic relevance.[25–27] It seems that no study on the possible role of metal hexacyanochromates(III) in chemical evolution has been touched. In this paper we report the results of our studies on the interaction of 5′-ribonucleotides with cobalt(II) and cadmium(II) hexacyanochromates(III).

Experimental

Chemicals. Potassium dichromate (B.D.H.), acetic acid (E. Merck), potassium cyanide (Loba Chemie), cobalt(II) nitrate (E. Merck), cadmium(II) nitrate (E. Merck), 5′-AMP (SRL), 5′-CMP (SRL), 5′-GMP (SRL), and 5′-UMP (SRL) were used as received. All other chemicals were of analytical reagent grade.

Preparation of Metal Hexacyanochromates(III). Both cobalt(II) and cadmium(II) hexacyanochromate(III) were synthesized from potassium hexacyanochromate(III), which was synthesized using Christensen's method.[28] To synthesize potassium hexacyanochromate(III), 25 g of potassium dichromate was dissolved in 500 mL of water and SO_2 gas was passed through it 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 so that chromium(III) hy-

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droxide precipitated. The gray-green colored chromium(III) hydroxide precipitates thus formed were filtered, 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 with caution so that the solution did not bump. It was then poured into a flask containing a boiling solution of 75 g of potassium cyanide in 300 mL of water. The reaction mixture was cooled, filtered, evaporated to 300 mL and filtered again. On cooling the mother liquid, pale-yellow needles of potassium hexacyanochromate(III) were obtained, which were washed and recrystallized.

Both the cobalt(II) and cadmium(II) hexacyanochromates(III) were prepared using a double decomposition method. 167 mL of a 0.1 M solution of potassium hexacyanochromate(III) was slowly added to 500 mL of a 0.1 M solution of cobalt(II) nitrate or cadmium(II) nitrate, respectively, with constant stirring. The excess metal salts were used to improve the coagulation of the precipitate. The reaction mixtures were kept as such for 24 h. The precipitates so obtained were filtered, washed thoroughly with water and dried. The dried products were ground and sieved to 80-mesh size. CHN analysis, X-ray diffraction, thermo gravimetric analysis, differential thermal analysis and infrared spectral studies of both the metal hexacyanochromates(III) were performed in order to test the purity of the complexes.

CHN Analysis. The percentage of carbon, nitrogen, and hydrogen in both metal hexacyanochromates(III) were recorded on an Elementar Vario ELIII CHNS analyzer. The data are shown in Table 1.

X-ray Diffraction Studies. The X-ray diffraction analysis of both powdered metal hexacyanochromates(III) was carried out using a Philips PW-1140/90 X-ray diffractometer. The relative-intensity data and interplanner spacing (d) values were in good agreement with the reported values,[26] as shown in Tables 2 and 3.

Spectral Studies. The electronic spectra of 5′-AMP, 5′-GMP, 5′-CMP, and 5′-UMP were recorded using a Shimadzu UV-16001 spectrophotometer and their characteristic values λ_{max} are 259, 254, 278, 262 nm, respectively. The infrared spectra of adsorbents, adsorbates and adsorption adducts were recorded in KBr discs on a Perkin Elmer FTIR spectrophotometer. Infrared spectral data of ribonucleotides and adsorption adducts are summarized in Tables 4 and 5.

Thermogravimetric and Differential Thermal Analysis. Thermograms for thermo gravimetric and differential thermal analysis of both hexacyanochromates(III) were recorded on a ther-

Table 1. Carbon, Hydrogen, and Nitrogen Analysis of Metal Hexacyanochromates(III)

Metal hexacyanochromates(III)	Carbon/%	Hydrogen/%	Nitrogen/%
$Cd_3[Cr(CN)_6]_2 \cdot 14H_2O$	13.94	2.74	15.83
	(14.34)[a)]	(2.79)	(16.33)
$Co_3[Cr(CN)_6]_2 \cdot 14H_2O$	16.78	3.44	18.43
	(17.04)	(3.31)	(18.88)

a) Bracket values are theoretical ones.

Table 2. X-ray Diffraction Data for Cobalt(II) Hexacyanochromate(III)

d/Å		I/I°	
Observed value	Reported value	Observed value	Reported value
5.16	5.18	78	80
3.67	3.66	100	100
2.59	2.59	82	80
2.32	2.31	61	60

Table 3. X-ray Diffraction Data for Cadmium(II) Hexacyanochromate(III)

d/Å		I/I°	
Observed value	Reported value	Observed value	Reported value
6.24	6.32	61	60
5.41	5.47	100	100
3.83	3.88	100	100
3.28	3.30	59	60
2.73	2.736	82	80
2.44	2.447	81	80
2.23	2.241	48	50

Table 4. Typical Infrared Spectral Frequencies (cm^{-1}) of Ribonucleotides before and after Adsorption on Cobalt(II) Hexacyanochromate(III)

Ribonucleotides	ν_{NH_2}		Typical of base residues		$\nu_{P=O}$	Typical of ribose residues	
5′-AMP	3104	3312	1574	1607	1086	1052	1135
	(3104)[a)]	(3326)	(1557)	(1610)	(1093)	(1045)	(1139)
5′-GMP	3105	3313	1688	1626	1090	1048	1139
	(3113)	(3335)	(1570)	(1625)	(1099)	(1035)	(1141)
5′-CMP	3103	3312	1586	1605	1089	1053	1138
	(3110)	(3337)	(1565)	(1609)	(1094)	(1046)	(1140)
5′-UMP			1650	1616	1092	1054	1136
			(1634)	(1611)	(1099)	(1048)	(1137)

a) Bracket values indicate typical infrared spectral frequencies after adsorption.

Table 5. Typical Infrared Spectral Frequencies (cm^{-1}) of Ribonucleotides before and after Adsorption on Cadmium(II) Hexacyanochromate(III)

Ribonucleotides	ν_{NH_2}		Typical of base residues		$\nu_{P=O}$	Typical of ribose residues	
5′-AMP	3104	3312	1574	1607	1086	1052	1135
	(3105)[a)]	(3324)	(1556)	(1611)	(1095)	(1047)	(1137)
5′-GMP	3105	3313	1688	1626	1090	1048	1139
	(3115)	(3335)	(1572)	(1623)	(1098)	(1041)	(1141)
5′-CMP	3103	3312	1586	1605	1089	1053	1138
	(3112)	(3340)	(1565)	(1608)	(1097)	(1048)	(1141)
5′-UMP			1650	1616	1092	1054	1136
			(1636)	(1613)	(1101)	(1048)	(1138)

a) Bracket values indicate typical infrared spectral frequencies after adsorption.

mogravimetric analyzer system STA-780 Series (Stantone Redcroft., U.K.). The heating rate was 10 °C/min. 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 12 water molecules in both the metal hexacyanochromates(III).

Adsorption Studies. The adsorption of all four ribonucleotides on both the metal hexacyanochromates(III) was studied at pH 4.0, 7.0, and 9.0 by adding 5 mL of 2.8×10^{-4} M ribonucleotide solutions to 25 mg adsorbent each time. The mixtures were shaken and their pH was adjusted to the desired value by adding a small amount of NaOH or HCl solution. The suspensions were shaken using an Expo shaker initially for 1 h and then allowed to equilibrate at 30 °C with intermittent shaking. After 24 h, the suspensions were centrifuged at 8000 rpm on a Remi centrifuging machine (model-220/230V 50–1Ø AC), manufactured by Remi Motors, Mumbai India, and the supernatant liquids were decanted. Ribonucleotide concentrations were determined spectrophotometrically. The amount of ribonucleotides adsorbed was estimated from the difference between their concentrations before and after adsorption. The equilibrium concentration of the ribonucleotides and the amounts adsorbed were used to obtain adsorption isotherms. The pH of the supernatant liquids was recorded on a pH meter (model CL-46, manufactured by Toshniwal Inst. Mfg. Pvt. Ltd., Ajmer) and was found to be nearly unchanged.

Results and Discussion

The preliminary studies on adsorption of ribonucleotides with cobalt(II) and cadmium(II) hexacyanochromates(III) were carried out over a wide pH range (4.0–9.0), and subsequent studies were performed at neutral pH (7.0), which showed the maximum adsorption for both the metal hexacyanochromates(III).

Adsorption can be correlated with the presence of negative charge on the phosphate group. At lower pH, adsorption is relatively lower. It may be due to the fact that nucleotide molecules possess both a negative as well as a positive charge at lower pH. But as the pH increases, the negative charge on the molecule increases. At neutral pH, 5′-monophosphate nucleotides exist in dianionic form as both the protons of the phosphate group are dissociated, so they may exhibit relatively higher adsorption. The pK_{2a} values for 5′-AMP, 5′-GMP, 5′-CMP, and 5′-UMP are 6.1, 6.1, 6.3, and 6.4, respectively.[32] It has been reported that dianionic nucleotides form stronger complexes with transition metal cations than monoionic nucleotides.[33] At higher pH, adsorption is less, which may be due to the competitive interaction of available $^-$OH with metal hexacyanochromate(III). The effect of pH on the adsorption of ribonucleotides on metal hexacyanochromates(III) is shown in Figs. 1 and 2.

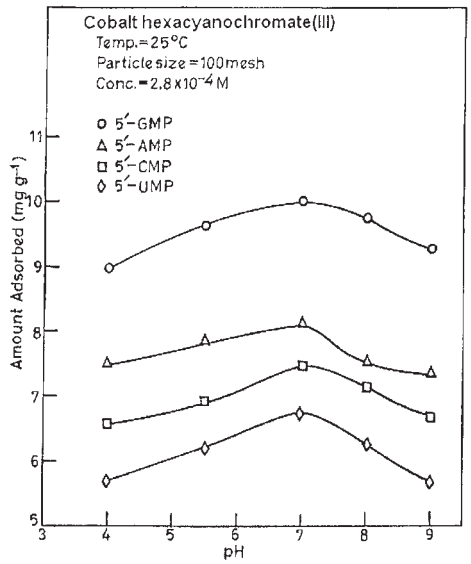

Fig. 1. Adsorption of ribonucleotides on cobalt(II) hexacyanochromate(III) as a function of pH.

For hexacyanochromates(III) of divalent metal ions, the general formula $M_3[Cr(CN)_6]_2 \cdot nH_2O$ has been reported, where M represents an exchangeable divalent transition metal ion. The $[Cr(CN)_6]^{3-}$ anion possess an octahedral geometry in which Cr^{3+} is surrounded by six CN^- ligands[30] and has the electronic configuration t_{2g}^3. One of the t_{2g} orbitals has two electrons, a second one an unpaired electron, whereas the third remains empty. This is because the electrons are filled against Hund's rule in the presence of cyanide ion, like other strong field ligands. Although CN^- bonds with Cr through σ donation, Cr donates π electrons present in its dπ orbital to the antibonding pπ orbital of CN^- resulting in sufficient back bonding character. The transition metal hexacyanochromates(III) generally exist in a polymeric lattice structure with $[Cr(CN)_6]^{3-}$ anions, in which another transition metal ion may be coordinated through the nitrogen end of the cyanide ligand. Detailed studies on the structure of metal hexacyanochromates(III) with the general formula $M_3[Cr(CN)_6]_2 \cdot nH_2O$ have been carried out by Ludi and Gudel.[31]

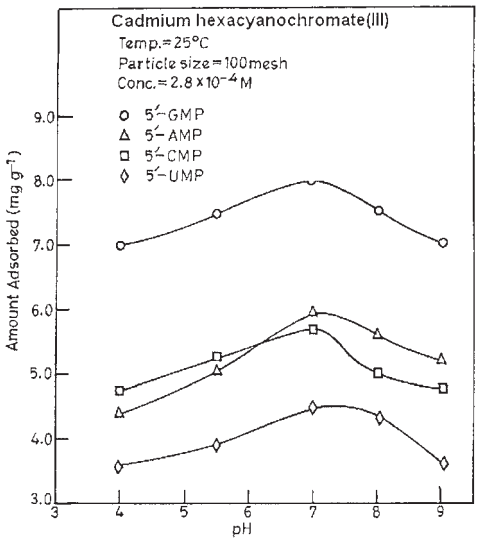

Fig. 2. Adsorption of ribonucleotides on cadmium(II) hexacyanochromate(III) as a function of pH.

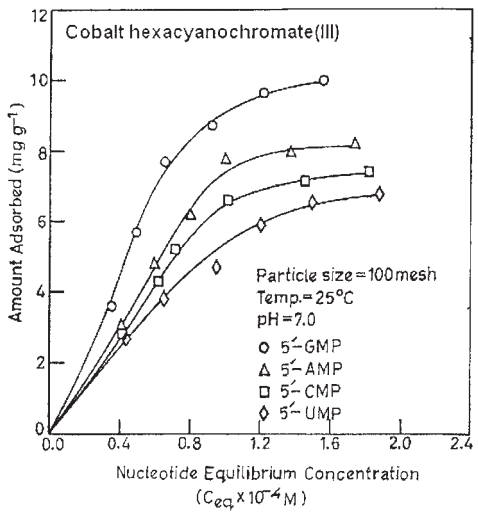

Fig. 3. Adsorption of ribonucleotides on cobalt(II) hexacyanochromate(III).

The adsorption data obtained at neutral pH (7.0) and over a wide concentration range of adsorbate (4×10^{-5} M to 2.8×10^{-4} M) was found to correlate with Langmuir adsorption isotherms, shown in Figs. 3 and 4. The initial portion of the isotherms represents a linear relationship between the amount adsorbed and the equilibrium concentration of the ribonucleotides. At a higher concentration range, the isotherms showed a saturation phenomenon indicating no further adsorption. The adsorption data were fitted with the Langmuir adsorption equation:

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

or

$$\frac{1}{X_e} = \frac{1}{C_{eq}}\left(\frac{1}{K_L X_m}\right) + \frac{1}{X_m} \quad (2)$$

where C_{eq} = equilibrium concentration of ribonucleotides,

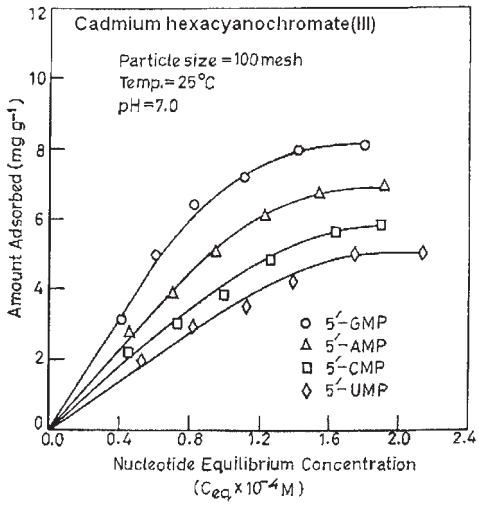

Fig. 4. Adsorption of ribonucleotides on cadmium(II) hexacyanochromate(III).

K_L = a constant related to the enthalpy (ΔH) of adsorption ($K_L \alpha e^{-\Delta H/RT}$), X_e = amount (mg) of solute adsorbed per gram of adsorbent, X_m = amount (mg) of adsorbate required per gram of adsorbent for complete monolayer formation.

The percent binding data, K_L and X_m values were determined and are shown in Tables 6 and 7, respectively, which indicate that 5′-GMP showed a maximum and 5′-UMP showed a minimum adsorption on both metal hexacyanochromates(III) studied. Cobalt(II) hexacyanochromate(III) showed a greater adsorption affinity towards all four ribonucleotides. The trend in adsorption of 5′-ribonucleotides for both metal hexacyanochromates(III) was found as:

$$5'\text{-GMP} > 5'\text{-AMP} > 5'\text{-CMP} > 5'\text{-UMP}. \quad (3)$$

It seems that the binding sites of nucleotides may be N-1 and N-9 for 5′-AMP, N-1 and N-7 for 5′-GMP, N-3 for 5′-CMP, and N-1 or N-3 for 5′-UMP. The adsorption is presumably related to the involvement of N-1, N-3, and N-7 of the base residues as well as to the dissociation of two available protons of the phosphate group. The presence of N-7 as an additional site available for interaction in cases of purine nucleotides may be responsible for their greater adsorption, therefore, 5′-AMP and 5′-GMP show greater adsorption than 5′-CMP and 5′-UMP at neutral pH. Pyrimidine nucleotides are able to form a complex through its phosphate moiety only, and purine nucleotides are able to form a bridging complex due to the availability of N-7 position present in addition to the phosphate moiety. In 5′-AMP and 5′-GMP, an amino group is present at the sixth and second positions, respectively, of the purine ring. In case of 5′-GMP, an amino group and phosphate moiety lie in the same plane and may be involved in the interaction. The amino group present in the cytidine ring of 5′-CMP may also be involved in the interaction.

The nature of the interaction between ribonucleotides and metal hexacyanochromates(III) can be discussed in terms of the infrared spectral studies. Ribonucleotide–metal hexacyanochromate(III) adducts were washed with water, dried, and then infrared spectra were recorded in a KBr disc. A shift towards higher wavelengths of the characteristic frequencies of ribonu-

Table 6. Percent Binding[a)] of Ribonucleotides on Metal Hexacyanochromates(III)

Metal hexacyanochromates(III)	5′-AMP	5′-GMP	5′-CMP	5′-UMP
Cobalt(II) hexacyanochromates(III)	34.25	41.56	32.17	28.62
Cadmium(II) hexacyanochromates(III)	24.66	30.52	24.25	23.42

a) % binding = {(O.D. before adsorption − O.D. after adsorption)/O.D. before adsorption} × 100.

Table 7. Langmuir Constants for Ribonucleotides Adsorption on Metal Hexacyanochromates(III)

Ribose nucleotides	Cobalt(II) chromicynide		Cadmium(II) chromicynide	
	X_m /mg g^{-1}	K_L /dm^3 mol^{-1}	X_m /mg g^{-1}	K_L /dm^3 mol^{-1}
5′-AMP	16.55	6.57	13.36	4.04
5′-GMP	18.82	8.28	14.20	8.27
5′-CMP	13.71	7.06	10.85	6.67
5′-UMP	12.72	6.51	10.07	4.76

cleotides was observed, which indicates an interaction between the ribonucleotides and metal hexacyanochromates(III). The characteristic infrared spectral frequencies are summarized in Tables 4 and 5. In the infrared spectra of ribonucleotides, typical strong bands in the region 950–1150 cm^{-1} are due to the presence of the ribose residue, and change negligibly after adsorption. This suggests that the ribose residue does not interact with metal hexacyanochromates(III). A remarkable shift was observed in the characteristic frequencies of the purine nucleus and phosphate group of ribonucleotides, which suggested a probable involvement of N-7 and the phosphate groups in the interaction of the 5′-ribonucleotides with the metal hexacyanochromates(III). Typical infrared frequencies of metal hexacyanochromates(III) were found to be almost unchanged, suggesting that the ribonucleotide molecules do not enter into the coordination sphere of metal hexacyanochromates(III) by replacing the cyanide ion. Further, insertion of ribonucleotide in the coordination sphere of a metal hexacyanochromate(III) is quite improbable, because CN^- can be substituted by other ligands only under UV light.[31] Thus, it seems that the interaction of ribonucleotides with metal hexacyanochromates(III) takes place through certain chemical forces. Ribonucleotides interact through their purine or pyrimidine residue and phosphate group with metal cations present in the lattice of metal hexacyanochromates(III).

The results of the present study support the postulate that metal cyanogen complexes could have provided a surface onto which biomonomers could have concentrated from their dilute aqueous solutions through adsorption processes during the course of chemical evolution. The biomonomers so concentrated would have been protected from degradation and might have undergone a reaction such as condensation, oligomerisation and/or polymerization to produce biopolymers. Thus, metal cyanogen complexes played an important role during the course of chemical evolution.

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