PREFERENTIAL UPTAKE OF AMMONIUM IONS BY ZINC FERROCYANIDE

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Abstract. The concentration of ammonia from dilute aqueous solution could have facilitated many prebiotic reactions. This may be especially true if this concentration involves incorporation into an organized medium. We have shown that (unlike iron(III) ferrocyanide) zinc ferrocyanide, $Zn_2 Fe(CN)_6 \cdot xH_2O$, preferentially takes up ammonium ions from 0.01 M NH_4Cl to give the known material $Zn_3(NH_4)_2[Fe(CN)_6]_2 \cdot xH_2O$, even in the presence of 0.01M KCl. KCl alone gave $Zn_3K_2[Fe(CN)_6]_2 \cdot xH_2O$. Products were characterized by elemental (CHN) analysis and powder X-ray diffraction (XRD). We attribute the remarkable specificity for the ammonium ion to the open framework of the product, which offers enough space for hydrogen-bonded ammonium ions, and infer that other inorganic materials with internal spaces rich in water may show a similar preference.

1. Introduction

For the Strecker synthesis of amino acids to be competitive with the production of hydroxyacids, the minimum concentration of the ammonium ion must be around 0.01 M, which places a possible lower limit on the ammonium ion concentration in the environment in which such amino acids could have been synthesized (Miller and van Trump, 1981). Without resorting to the hypothesis of a strongly reducing atmosphere, it is difficult to see how such concentrations of ammonia could have arisen. Ammonia can be generated by the reductive reaction of iron(II), certainly present in large amounts on the early Earth, with nitrite generated by atmospheric processes (Summers and Chang, 1994; Hansen *et al.*, 1994). However, it is readily decomposed by uv light (Ferris and Nicodem, 1972; Kasting, 1982). Any mechanism by which ammonia can be removed from aqueous solution, thus both concentrating and protecting it, is therefore of great interest in connection with the earliest stages of the processes leading to the origins of life.

It is generally accepted among chemists (see e.g. Gillespie *et al.*, 1994) that ammonium salts are soluble in water. Indeed, they are expected to be generally more soluble than those of the Group 1 elements, because of hydrogen bonding between the ammonium ion and water. However, Bellomo (1970) observed that the solubility product of $K_2Zn_3[Fe(CN)_6]_2$ is 5.5×10^{-39} ($\Delta G_o = -218$ kJ/mol),

while that for $Zn_2Fe(CN)_6$ is 1.5×10^{-17} ($\Delta G_o = -96$ kJ/mol), implying that the exchange of zinc for potassium in latter compound is thermodynamically favored. It occurred to us that, given this affinity of the zinc ferrocyanide system for univalent ions, there was a possibility that $Zn_2Fe(CN)_6$ would take up ammonium ions. We now report that this is the case, and that ammonium is actually taken up in preference to potassium at the concentration required for successful Strecker synthesis.

2. Experimental

All materials were Fisher certified or better, and were used without further purification. Water was from a Millipore milli-Q system, with a resistance of 18 Mohm cm^{-1}. Silica gel was recently re-heated self-indicating. Analyses were carried out by us on a Perkin-Elmer 2400 CHN analyzer at the Scripps Institution of Oceanography, using acetanilide as standard. X-ray diffraction was carried out using a General Electric XRD5 instrument with Philips monochromator, custom modified for digital data collection and handling.

Preparation of $Zn_2Fe(CN)_6 \cdot 4H_2O$: 1.093 g (4.98 mmol) $Zn(OAc)_2 \cdot 2H_2O$ and 1.613 g (19.8 mmol) ZnO were placed in a conical flask and treated with the acidic eluate formed by passing 50 mL water containing 3.815 g (9.03 mmol) $K_4Fe(CN)_6 \cdot 3H_2O$ through a column containing 60 ml (115 mEq) Amberlite IR 120 resin (acid form, freshly washed). This procedure was adopted to buffer the reacting mixture and minimize the length of time the ferrocyanide would be in the free acid form, since it was feared that this would lead to decomposition to Prussian Blue (ferric ferrocyanide). The procedure was presumably successful, since during the addition the pH in the flask dropped only to around 3, and then returned to neutral. A light blue coloration was observed in the first acid washings from the column, and the solid formed by the reaction had a very pale blue tinge. The slurry of product was decanted (leaving some excess coarse material, presumed excess ZnO, behind), washed 5 times by centrifugation, and dried in a vacuum desiccator over silica gel. Nominal yield 3.60 g (8.6 mmol, 96%) $Zn_2Fe(CN_6) \cdot 4H_2O$. The identity of the material was confirmed by powder x-ray diffraction (Fig. 1a). Investigation by electron microscopy and electron diffraction (V. Drits, private communication) revealed the presence of small amounts of unreacted ZnO; this would not affect the validity of our results.

Exchange of $Zn_2Fe(CN)_6 \cdot 4H_2O$ with NH_4Cl and with KCl: Four samples each of approximately 0.5 g (1.2 mmol) $Zn_2Fe(CN)_6 \cdot 4H_2O$ dispersed in a few mL water were treated with (A) 50 mL 0.1 M NH_4Cl, (B) 250 mL 0.01 M NH_4Cl, (C) 250 mL 0.01 M KCl (D) 250 mL of a solution 0.01 M in KCl and also 0.01 M in NH_4Cl, and left for two days. Materials were then washed twice with water by centrifugation, dried in a vacuum desiccator overnight over silica gel, and examined by elemental (CHN) analysis and by powder XRD.

TABLE I

Main X-ray diffraction peaks for
$Zn_3(NH_4)_2[Fe(CN)_6]_2 \cdot xH_2O$
(experiment A).

d-spacing (Å)	Peak height (Arbitrary units)
11.02	9
8.99	13
6.48	18
5.41	100
4.50	59
4.35	41
4.09	85
3.77	59
3.61	41
3.12	36
2.84	12
2.71	18
2.53	12

Preparation of $K_2ZnFe(CN)_6 \cdot 4H_2O$ was by direct reaction between $K_4Fe(CN)_6$ and $Zn(OAc)_2 \cdot 2H_2O$ in the molar ratio 1.03:1.

Preparation of potassium-free Prussian Blue, $Fe_4[Fe(CN)_6]_3$, was accomplished by eluting 4.223 g (10.0 mmol) $K_4Fe(CN)_6$ through Amberlite IR 120 resin as discussed above onto a nominal 4.114 g (15.2 mmol) (upper limit; material hygroscopic) $FeCl_3 \cdot 6H_2O$, followed by washing, and attempted exchange with ammonium and potassium ions, as for $Zn_2Fe(CN)_6 \cdot 4H_2O$ above.

3. Results and Discussion

The crystal structure of $Zn_2Fe(CN)_6 \cdot 4H_2O$ is not known; however, the x-ray diffraction pattern that we obtained for this material (Fig. 1a) agrees well with that reported by Siebert *et al.* (1981). The diffraction patterns for the materials obtained in exchange reactions A and C were very similar (Figs 1b, 1c; Tables I, II) and agreed well with the data of Garnier *et al.* (1982) for $Na_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$. These patterns are quite different from those reported by Rigamonti (1938), and confirmed by us during this work, for $K_2ZnFe(CN)_6$. Thus at our concentrations direct reaction of potassium ferrocyanide with zinc acetate gives a compound in the series $M(I)_2ZnFe(CN)_6$, but the reactions of zinc ferrocyanide with excess of either potassium or ammonium ions gives products in the series $M(I)_2Zn_3[Fe(CN)_6]_2$.

TABLE II

Main X-ray diffraction peaks for $Zn_3K_2[Fe(CN)_6]_2 \cdot xH_2O$ (experiment C).

d-spacing (Å)	Peak height (Arbitrary units)
9.05	8
7.80	8
6.47	17
6.27	17
5.42	100
4.51	48
4.30	15
4.08	100
3.79	49
3.62	33
3.11	25
3.00	12
2.81	13
2.71	13
2.52	17
2.47	19

TABLE III

Substance	%C	%N	%H[a]	C:N:H, found	C:N:H, calcd.
$K_4Fe(CN)_6 \cdot 3H_2O$	17.06	19.03	1.30	1:0.956:0.915	1:1:1
$(NH_4)_2Zn_3[Fe(CN)_6]_2 \cdot$	18.49	24.94	2.35	1:1.158:1.526	1:1.167:1.5
$5H_2O^a$: Sample A	18.47	25.32	2.45	1:1.176:1.592	
Sample B	18.45	24.94	2.27	1:1.160:1.477	
	18.33	24.70	3.01	1:1.160:1.971	
Sample D	17.98	24.04	2.04	1:1.147:1.362	
	18.06	23.52	2.24	1:1.118:1.489	
$K_2Zn_3[Fe(CN)_6]_2 \cdot 8H_2O^a$	17.64	20.28	1.85	1:0.987:1.259	1:1:1.25
$Zn_2Fe(CN)_6 4 \cdot 5H_2O^a$	16.66	19.33	2.12	1:0.987:1.515	1:1:1.5

[a] For the zinc ferrocyanides, hydrogen analyses and nominal degrees of hydration are included for completeness only.
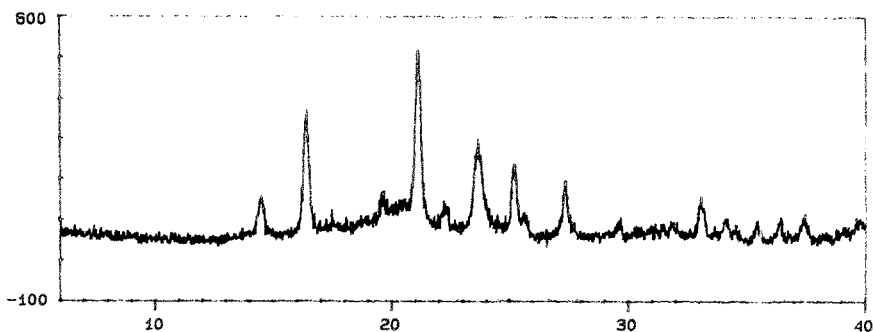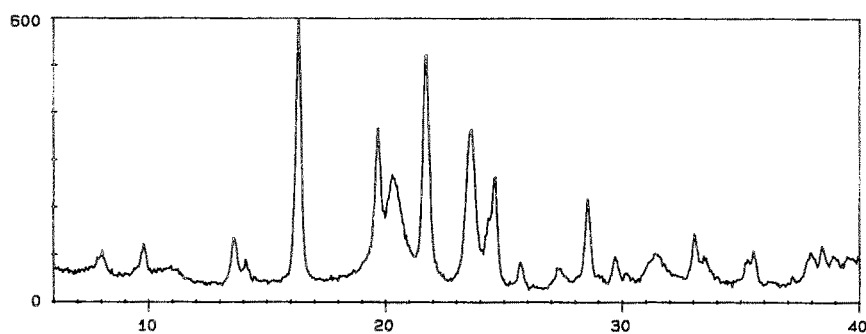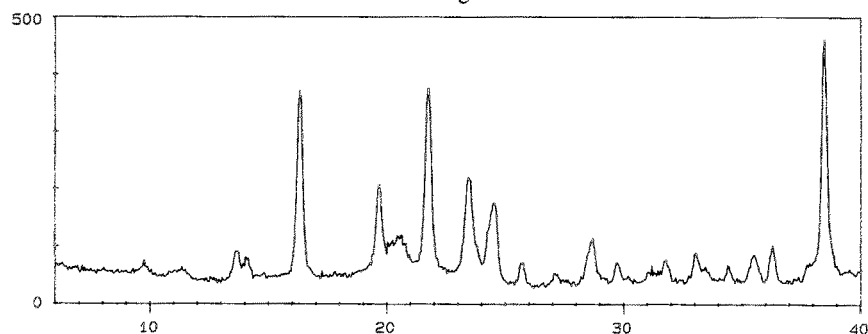
Fig. 1a.

Fig. 1b.

Fig. 1c.

Figs. 1(a)–(c). Powder x-ray diffraction patterns of parent and exchanged zinc ferocyanides: (a) Parent material, $Zn_2FE(CN)_6 \cdot xH_2O$; (b) parent after exchange with ammonium ions (experiment A), giving $Zn_3(NH_4)_2[Fe(CN)_6]_2 \cdot xH_2O$; (c) parent after exchange with potassium ions (experiment C), giving $Zn_3K_2[Fe(CN)_6]_2 \cdot xH_2O$.

Loos-Neskovic, Fedoroff *et al.* have examined and reviewed the structural and ion exchange chemistry of the zinc ferrocyanides in some detail (1984, 1989). Both $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ and $(NH_4)_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ are known compounds. $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ has been prepared both by direct synthesis, and by

exchange of $Zn_2Fe(CN)_6 \cdot 4H_2O$ with potassium ions. $(NH_4)_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ has been prepared by reaction of zinc sulfate with ammonium ferrocyanide, but its formation by exchange of $Zn_2Fe(CN)_6 \cdot 4H_2O$ with ammonium ions has not to our knowledge been reported before.

Analytical data for the relevant materials are given in Table III. It is clear that for samples A, B, and D, the C:N atomic ratio is equal within experimental error to the formulation $(NH_4)_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$. [The slightly lower proportion of N in Sample D probably reflects minor competition between potassium and ammonium. The result is at the limits of observation, but small amounts of potassium are detectable in the EDX signal from this material.] However, $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ (sample C), $K_2ZnFe(CN)_6 \cdot xH_2O$, and $K_4Fe(CN)_6 \cdot 3H_2O$ all give C:N atomic ratios of 1:1, thus validating the method. We conclude that zinc ferrocyanide reacts quantitatively to remove ammonium ions from aqueous solution, even when their concentration is as low as 0.01 M before uptake, falling in experiments B and D to 0.005 M after making allowances for the removed ions. Moreover, the reaction proceeds preferentially even in the presence of potassium ions, although as the XRD data show the uptake of potassium ions alone is also essentially complete under the same conditions. We include for completeness data for H, with idealized formulas for hydration, but we attach no great significance to these.

These results can perhaps be understood by reference to the crystal structure of $Na_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ (Garnier, Gravereau and Hardy, 1982). In this structure, the ferrocyanide units retain their identity as expected; each zinc is tetrahedrally coordinated by N (so that all ferrocyanide nitrogens are acting as ligands to zinc); and sodium ions and water are shared over sites in the large cavities present in the resulting framework. We propose that these cavities can also be occupied by hydrated ammonium ions. This interpretation is consistent with the observed failure of iron(III) ferrocyanide to exchange with ammonium ions in this work.

4. Conclusions

We have shown that ammonium ions can be taken up from dilute solutions by zinc ferrocyanide. Given the availability of Fe(II), the generally non- oxidizing conditions, and the ease with which the insoluble transition metal ferrocyanides are formed, this is not a completely implausible material to have been found on the early Earth. A requirement would, however, have been that sufficient amounts of cyanide were present, and that complex formation of cyanide with Fe^{2+} could compete with the formation of cyanohydrin from formaldehyde (Arrhenius et al., 1994). This work should also be compared with that of Kamaluddin et al. (1990), who report adsorption of amino acids by metal ferrocyanides. While such materials do not occur as minerals at present, their occurrence on the early Earth, given the availability of iron(II) and its high affinity for cyanide, should not be too readily

excluded. However, in our opinion the chief importance of the present work lies in the general proposition that ammonium ions can be concentrated in environments that favor large cations and allow for hydrogen bonding to water. This may have implications, not only for the accumulation of ammonia on the early Earth, but on its availability to take part in reactions on the internal and external surfaces of solids, as required by more than one model of the origins of biologically significant materials. As an example, common lamellar metal hydroxide minerals, such as magnesium aluminum hydroxide (hydrotalcite), readily exchange chloride or sulfate ions in the hydrated interlayer against higher charge density anions such as $[Fe(CN)_6]^{4-}$ (see e.g. Kuma *et al.*, 1989; Arrhenius *et al.*, 1993). Excess negative charge on these is balanced by association with cations such as potassium or ammonium, whose presence in the mineral interlayer has been ascertained by spectroscopic measurements. Indeed, we have already obtained spectroscopic evidence for the incorporation of ammonium ions into the water-rich interlayer spacing that results when magnesium aluminum hydroxide chloride is exchanged with ammonium ferrocyanide. The greatest interest would attach to systems which bond strongly enough to the ammonium ion to concentrate it, but not so strongly as to render it unavailable for further reaction. For this reason, the availability for reactivity of the ammonium ions incorporated into the magnesium aluminum hydroxide ferrocyanide system is currently under investigation.

Acknowledgements

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