

Hydration Reaction of Hofmann's Benzene Clathrate, Diamminenickel(II) Tetracyanonickelate(II)-Benzene - (1/2), Suspended in Aqueous Media

ISAMU UEMASU and TOSCHITAKE IWAMOTO*

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

(Received: 21 December 1982)

Abstract. Hofmann's benzene clathrate $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ suspended in ammoniacal, neutral, and acidic aqueous media undergoes the replacement reactions of the guest C_6H_6 and the ligating NH_3 molecules with molecules of water to give $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$, $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ ($0 < n < 2$), and $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4 \sim 5\text{H}_2\text{O}$, respectively. The integrity of the host metal complex sheet structure is conserved with little change during the replacement reactions.

Key words: Hofmann-type clathrate, guest-replacement reaction, nickel(II) cyanide hydrate.

1. Introduction

The Hofmann-type clathrates $\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{G}$ can be seen as intercalation compounds formed between two dimensionally-extended metal complex sheets and aromatic guest molecules enclathrated between the sheets [1]. The sheet consists of a square-meshed network of the square-planar $\text{M}'(\text{II})$ and the six-coordinate $\text{M}(\text{II})$ metals alternately bridged with the ambidentate CN^- ligands of the square-planar tetracyanomethylate ($\text{M}'(\text{II})$) moieties; the six-coordination of $\text{M}(\text{II})$ is accomplished by four nitrogen-ends of the CN^- ligands and two nitrogens of a pair of NH_3 ligands in a *trans* configuration. Thus, each sheet has NH_3 ligands protruding up and down at each $\text{M}(\text{II})$ atom in the network. The aromatic guest molecule G, such as pyrrole, thiophene, benzene, etc., is trapped between the sheets with its aromatic plane vertical to the sheets. The distance between adjacent sheets depends on the size of the guest molecule. For example, the largest distance (12.65 Å) has been observed for the biphenyl clathrate and the smallest (7.89 Å) for the pyrrole one in Hofmann's host $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4$ [2], in which both the M and M' in the general formula are Ni. Evidence has been found that anhydrous nickel(II) cyanide has a layered structure, similar to that observed for the host structure of Hofmann's clathrate $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{G}$, except for the lack of an NH_3 protrusion between the sheets. Absorption of long-chain *n*-alkylamines, alcohols, or nitriles makes nickel(II) cyanide swell by the formation of intercalation compounds of these organic molecules in the layered structure [3,4]. From the view-point of intercalation chemistry, the enclathrated C_6H_6 molecules in, and the coordinating NH_3 ligands protruding into the interlayer space in Hofmann's benzene clathrate are the intercalated species in the layered structure of nickel(II) cyanide. The purpose of this

* Addressee for correspondence.

investigation is to examine the exchange or replacement of the intercalated species in the heterogeneous reactions of Hofmann's benzene clathrate suspended in aqueous media. In the suspensions examined, the solid $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ clathrate first lost the guest C_6H_6 molecules, and then finally the NH_3 ligands, to give, respectively $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \approx 1\text{H}_2\text{O}$ and two kinds of nickel(II) hydrates: $\text{Ni}(\text{CN})_2 \cdot m\text{H}_2\text{O}$ ($= \text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$, $n = m - 2$) with different hydration numbers.

2. Experimental

The benzene clathrate $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ used in this experiment was prepared as fine crystals by leaving the ammoniacal solution of nickel(II) chloride and potassium tetracyanonickelate(II) in contact with the organic phase of benzene diluted with xylene for a few days in a refrigerator. About 100 mg each of the specimens prepared by grinding the fresh crystals in an agate mortar were suspended in *ca.* 50 mL of $\text{NH}_3 - \text{NH}_4\text{Cl}$ buffer solution at pH 10, in distilled water, or dil. HNO_3 . The hydrated products were recovered by filtration from the suspensions after having been stirred by a magnetic stirrer for a few days at room temperature. The solid materials recovered were washed with water and ethanol successively, and air-dried; the recovery, of more than 60% was obtained based on the Ni content in the solid. The products were identified by chemical analysis, powder X-ray diffractometry, and infrared spectroscopy.

Diamminenickel(II) tetracyanonickelate(II) hydrate [5] and diaquanickel(II) tetracyanonickelate(II) hydrates [6, 7] were prepared as the reference materials by the methods given in the literature.

3. Results and Discussion

The total reaction schemes are shown in Figure 1, and the structural data of the related compounds are tabulated in Table I. The illustrative models of their structures are shown in Figure 2.

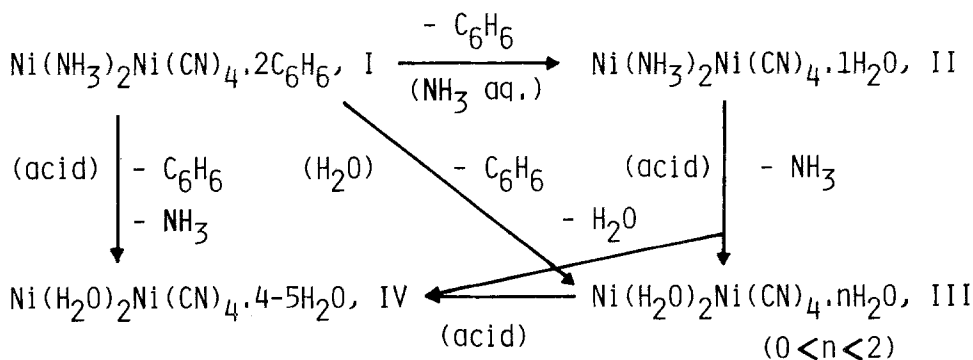


Fig. 1. Schemes of Hydration Reactions.

3.1. REACTION IN AMMONIACAL SOLUTION

The clathrate $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, I, dissolves completely in the $\text{NH}_3 - \text{NH}_4\text{Cl}$ buffer solution, unless the concentration of NH_3 is less than 1 mol L^{-1} . Therefore, the NH_3 concentration was kept at 0.5 mol L^{-1} in the suspending buffer solution. After a lapse of time,

TABLE I. Structural data of Hofmann's benzene clathrate and its hydrates

		Space group	Crystal system	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	Z	$d/\text{\AA}^a$
I	$\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$	$P4/m$	tetragonal	7.242	$= a$	8.277	1	8.277
II	$\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	$Imma$	orthorhombic	7.24	14.32	8.74	4	4.37
III	$\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ ($0 < n < 2$)		orthorhombic	7.26	14.20	8.88	4	4.44
IV	$\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ ($n > 3$)		orthorhombic	7.09	13.84	6.10	2	6.10
V	$\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4^b$	$I4_1/amd$	tetragonal	7.222	$= a$	17.42	4	4.36

^a Interlayer distance between adjacent metal cyanide sheets.

^b Listed for the sake of comparison.

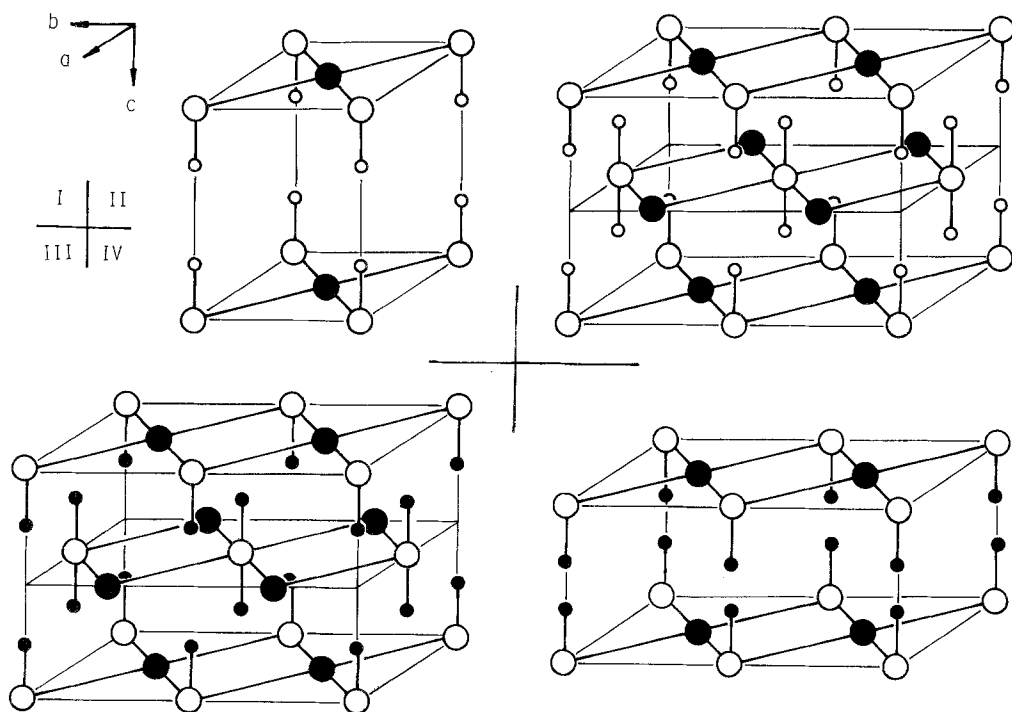


Fig. 2. Illustrative Structural Models of I: $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, II: $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \approx 1\text{H}_2\text{O}$, III: $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ ($0 < n < 2$), and IV: $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4 \sim 5\text{H}_2\text{O}$. Large open circle: six-coordinated Ni, large solid circle: square-planar Ni, small open circle: N of NH_3 , small solid circle: O of coordinated H_2O . The benzene molecule in I, C and N of CN^- , protons of NH_3 and H_2O , and enclathrated water molecules are omitted.

the guest benzene molecules in I are replaced by water molecules, as indicated by the change in the powder X-ray diffraction patterns from that of I to that of a mixture of I and $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ [5]. After 24 hr of stirring, the trace of the bands due to C_6H_6 in the clathrate disappeared in the infrared spectrum of the recovered solid. The solid identified as $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \approx 1\text{H}_2\text{O}$, II, based on the acceptable coincidence of the infrared spectrum and the powder X-ray diffraction pattern with those of the diamminenickel(II) tetracyanonickelate(II) hydrate prepared independently. The number of water molecules was

estimated to be ≈ 1 from the results of chemical analysis. Found: Ni, 42.5; C, 17.02; H, 2.18; N, 28.04%. Calcd. for $\text{Ni}_2\text{C}_4\text{H}_{10}\text{N}_6\text{O}$: Ni, 42.5; C, 17.56; H, 2.95; N, 30.73%. The variation from $\frac{1}{2}$ in the original literature to ≈ 1 can be interpreted in terms of the non-stoichiometric character of the enclathrated water molecules as has been described by Rayner and Powell [5].

3.2. REACTION IN DISTILLED WATER

The specimen of **I** suspended in distilled water lost the benzene molecules completely after 12 hr of stirring. The infrared spectrum showed the bands due to H_2O at 3590 cm^{-1} and 1610 cm^{-1} of an intensity considerably stronger than those observed for **II**, whereas the band at *ca.* 1230 cm^{-1} due to NH_3 was present in weak intensity. The powder diffraction pattern was almost identical to that of **II**. However, it was concluded that the main product was not **II** but $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ ($0 < n < 2$), **III**, for the following reasons. First, the analytical results showed an N content smaller than that calculated for **II**. From the values, Ni, 43.4; C, 17.04; H, 2.45; N, 23.33%, the atomic ratio Ni:C:N was given as 1:2:2.3. Since the ratio for **II** is 1:2:3, the main product cannot be **II**. Ludi and Hügi [6], and Mathey and Mazieres [7] reported on several species and phases of nickel(II) cyanide hydrates $\text{Ni}(\text{CN})_2 \cdot m\text{H}_2\text{O}$ with various values of m and concluded that these hydrates are formulated as $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ ($n = m - 2$). Among them one can discover an orthorhombic phase, $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ ($0 < n < 2$) [7], which can be assigned to **III**, with lattice parameters similar to those of **II** (Table I). The larger N content than that calculated for **III** (Ni:C:N = 1:2:2) can be attributed to the incomplete replacement of the NH_3 ligands in **II**, since the band due to NH_3 at 1230 cm^{-1} did not completely disappear in the infrared spectrum.

3.3. REACTION IN ACIDIC SOLUTION

The specimen of **I** suspended in dil. HNO_3 turned to $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ ($n > 3$), **IV**, when the molar amount of HNO_3 was more than twice that of NH_3 in the original **I**. Any infrared bands due to NH_3 and C_6H_6 disappeared completely and the powder X-ray diffraction pattern was identified with that of **IV**, as reported by Mathey and Mazieres [7]; the value of n was estimated to be $4 \sim 5$ from the analytical results, Ni, 34.0; C, 14.28; H, 3.71; N, 16.53%. When the amount of acid was insufficient to neutralize the NH_3 in **I**, (for example, 82% of the molar amount of NH_3) the product was a mixture of **II**, **III** and **IV**, judging from the infrared spectrum and the powder X-ray diffraction pattern. The independently-prepared **III** changed to **IV** on suspension in dil. HNO_3 , whereas the independently-prepared **II** did not completely change to **IV** under similar conditions.

3.4. DISCUSSION

Single crystal structure determinations have been performed for **I** [8] and **II** [5], and the lattice parameters are available for **III** and **IV** [7]. These suggest the structures of the respective hydrates, as shown in Figure 2, although the orientation of the intercalated water molecules is not known in detail for **II**, **III**, and **IV**. According to the reaction schemes in Figure 1, the hydration reaction proceeds by the stepwise replacement of the guest molecules and the ammine ligands by water molecules. As has been pointed out by Rayner and Powell [5], the hydration of **I** occurs even on the surface of the single crystals left under ambient atmosphere.

Upon hydration, the host metal complex sheet shifts by $(a + b)/2$ with a distortion from the tetragonal symmetry of **I** to orthorhombic, and the interlayer distance decreases from 8.28 to 4.37 Å. Rae and Maslen [9] analyzed the crystal structure of anhydrous diamminenickel(II) tetracyanonickelate(II) $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4$, **V**, in which the interlayer distance was reported to be 4.36 Å. It is rather difficult to interpret the similar distances for **II** and **V**, despite the fact that the former contains non-stoichiometric 'enclathrated' water molecules, whereas **V** does not.

When the medium is neutral or slightly acidic, as is usual in distilled water, the benzene molecule is lost, followed by successive replacement of ammine ligands by water to give **III**. The interlayer distance is similar to that in **II** and the cyanide network keeps the $(a + b)/2$ shift with the orthorhombic symmetry. When the medium is acidic, the layered structure swells again, with expansion from ca. 4.4 Å in **II** and **III** to 6.10 Å, by enclathrating more water molecules between the host layers, and the $(a + b)/2$ shift is recovered.

Throughout these replacement processes, the layered structure of the cyanide network is conserved with little change, except for the distortion from the tetragonal symmetry in **I** to the orthorhombic symmetry of **II**, **III**, and **IV**.

Hofmann-type clathrates usually give the nearly stoichiometric composition $\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{G}$, when well-developed crystals are analyzed. However, the finely powdered products prepared by vigorously mixing the aqueous solution of host moieties and the organic phase of guest species often give rather non-stoichiometric compositions. The reason why the powdery products are non-stoichiometric can be interpreted in the following terms. First, the clathrate, once formed, successively undergoes a hydration reaction, which is accelerated by the larger specific surface area: secondly, the formation of the hydrated metal complex appears to be competitive with that of clathrate formation under these conditions. The problems in measuring infrared spectra of Hofmann-type clathrates have been attributed to the partial hydration which occurs in pasting the specimen with Nujol [10, 11]; the origin of the water molecules has been assumed to be atmospheric water and/or water contained in the Nujol as an impurity. The specious composition of the so-called 'hydrated' clathrate $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \frac{2}{3}\text{H}_2\text{O} \cdot n\text{G}$ ($n = 1/20 \sim 1/2$) [12] was caused by the competitive formation of the hydrate with respect to the aromatic guest clathrate. In discussions of clathrate compounds of this type, careful attention should be paid to structural considerations in addition to the analytical data.

Acknowledgement

This work was partially supported by Grant-in-Aid for Scientific Research No. 56540357 from the Ministry of Education, Science and Culture.

References

1. T. Iwamoto: *J. Mol. Struct.* **75**, 51 (1981).
2. T. Iwamoto: *Isr. J. Chem.* **18**, 240 (1979).
3. G. F. Walker and D. G. Hawthorne: *Trans. Faraday Soc.* **63**, 166 (1966).
4. A. Weiss and R. Frank: *Kolloid-Z.* **177**, 47 (1961).
5. J. H. Rayner and H. M. Powell: *J. Chem. Soc.* 3412 (1958).
6. A. Ludi and R. Hügi: *Helv. Chim. Acta*, **50**, 1283 (1967).
7. Y. Mathey and C. Mazieres: *Can J. Chem.* **52**, 3637 (1974).

8. J. H. Rayner and H. M. Powell: *J. Chem. Soc.* 319 (1952).
9. A. I. M. Rae E. N. Maslen: *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **123**, 391 (1966).
10. S. Akyuz, A. B. Dempster, R. L. Morehouse, and N. Zegin: *J. Chem. Soc., Chem. Commun.* 307 (1972).
11. S. Akyuz, A. B. Dempster, and R. L. Morehouse: *Spectrochim. Acta, Part A* **30**, 1989 (1974).
12. R. S. Drago, J. T. Kwon, and R. D. Archer: *J. Amer. Chem. Soc.* **80**, 2667 (1958).