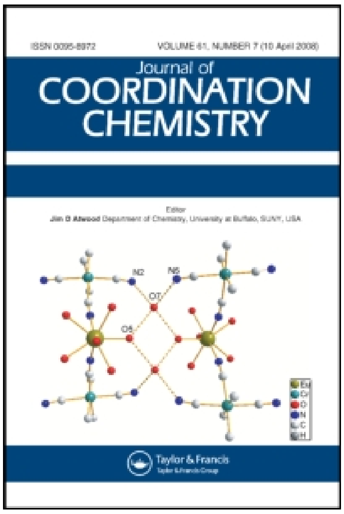

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SYNTHESES OF CYANOMETAL INCLUSION COMPOUNDS (PART I): PREPARATION AND CHARACTERIZATION OF *catena*-[*catena*-(α,ω)-DIAMINOHEXANE)CADMIUM-μ-TETRACYANONICKELATE]-χGUEST COMPLEXES

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Synthetic details of a series of clathrate compounds of general formula, *catena*-[*catena*-(α,ω-diaminohexane)cadmium-μ-tetracyanonickelate]-χGuest, are described. The coefficient χ, *i.e.* the number of guest molecules per unit of the host metal complex, is estimated for each complex. The features of this type clathrate are discussed.

KEYWORDS: clathrate, diaminohexane, Hofmann-type, cyanometal, tetracyanonickelate, non-stoichiometric

INTRODUCTION

A clathrate is a microcosm where each guest molecule has segregated small space. In the 1970's Iwamoto named a series of clathrates with the general formula $M(NH_3)_2M'(CN)_4 \cdot 2G$ as Hofmann-type clathrates after a German chemist who reported the prototype compound in 1897. A number of novel host structures have been derived from the original Hofmann-type host by replacing the square-planar tetracyanometallate(II) by tetrahedral one such as $Cd(CN)_4{}^{2-}$ or $Hg(CN)_4{}^{2-}$ and replacing a pair of the ammine ligands by ambident diamines. One of the attempts was to use diaminoalkanes with a carbon-chain length longer than that of ethylenediamine in order to extend the interlayer distance between the cyanometal complex network layers spanned by the diamine and to increase the lipophilic character of the cavity for the guest molecules.

During study of Hofmann-diaminoalkane-type compounds, Hofmann-diaminohexane complexes proved to be rich in structural chemistry[1–4] as well as Hofmann-diaminooctane-type[5–7] and Hofmann-diaminononane-type complexes.[8,9] Here we present the detailed description of the syntheses of the Hofmann-diaminohexane-type complexes,[10] which were reported preliminarily.[11]

Dedication Dedicated to Dr. Toschitake Iwamoto on his 60th birthday. Taken in part from T. Hasegawa, D.Sc. Thesis, University of Tokyo, 1986.

EXPERIMENTAL

Analyses

Routine microanalyses were performed at the microanalytical laboratories at the Department of Chemistry, Faculty of Science, the University of Tokyo; RIKEN; Sagami Research Center; and the Department of Pharmaceutical Chemistry, Faculty of Pharmaceutical Science, the University of Tokyo. When routine analyses were not sufficient, special analyses were performed using atomic absorption spectroscopy, thermoanalyses, and titration methods at the Department of Chemistry, College of Arts and Sciences, the University of Tokyo.

Syntheses

Host solution (**1**)

To an aqueous solution (200 mL) containing an equimolar mixture of $CdCl_2$ (20 mmol) and $K_2[Ni(CN)_4]$ (20 mmol), a two-fold molar amount of 1,6-diaminohexane (40 mmol) was added and mixed vigorously by a magnetic stirring bar for a few hours. After the pH of the aqueous phase was adjusted to 9.5 using citric acid (13 g) and monoethanol amine (9 mL), the mixture was filtered through a plastic membrane (Millipore filter with a pore size 0.45 μm) to remove impurities. This filtrate, **1**, was used in the following procedures.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-fluorobenzene

In a stoppered flask, **1** (pH 9.62) was covered with neat fluorobenzene, and the flask was left for a few days at room temperature (*ca.* 293 K). Fine yellowish crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-chlorobenzene

In a stoppered flask, neat chlorobenzene was placed under **1** (pH 9.62), and the flask was left for a few days at room temperature (*ca.* 293 K). Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-bromobenzene

In a stoppered flask, neat bromobenzene was placed under **1** (pH 9.71), and the flask was left for a few days at room temperature (*ca.* 293 K). Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-iodobenzene

In a stoppered flask, neat iodobenzene was placed under **1** (pH 9.62), and the flask was left for a few days at room temperature (*ca.* 293 K). Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-toluene

In a stoppered flask, **1** (pH 9.14) was covered with neat toluene, and the flask was left for a few days at 278 K. Yellowish plate-like crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-aniline

In a stoppered flask, **1** (pH 9.64) was covered with a mixture of aniline and mesitylene (1:5 v:v), and the flask was left for a few days at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-phenol

In a stoppered flask, **1** (pH 9.62) was covered with a solution composed of phenol and mesitylene (1:6 w:w) and the flask was left for a few days at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and the organic phases. A homogeneous solution made by mixing **1** and a 1:2 phenol-ethanol solution also gives the same product after a few days at room temperature.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-nitrobenzene

In a stoppered flask, neat nitrobenzene was placed under **1** (pH 9.62), and the flask was left for a few days at room temperature. Yellowish crystals were formed at the interface between the aqueous and organic phases. We have not confirmed the components of this compound.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-ethylbenzene

In a stoppered flask, **1** (pH 9.62) was covered with neat ethylbenzene, and the flask was left for a few days at room temperature. Yellowish crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-styrene

In a stoppered flask, **1** (pH 9.62) was covered with neat styrene, and the flask was left for a few days at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-phenylacetylene

In a stoppered flask, **1** (pH 9.62) was covered with neat phenylacetylene, and the flask was left for a few days at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-N,N-dimethylaniline

In a stoppered flask, **1** (pH 9.71) was covered with 1:5 N,N-dimethylaniline-mesitylene mixed solution, and the flask was left for a few days at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-o-Toluidine

In a stoppered flask, **1** (pH 10.20) was covered with a 1:5 o-toluidine-mesitylene mixed solution, and the flask was left for a few days at room temperature. Yellowish cubic crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-m-toluidine

In a stoppered flask, a 1:10 m-toluidine-mesitylene mixed solution was placed over **1** (pH 9.62), and the flask was left for two months at room temperature. Yellowish cubic crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-p-toluidine

In a stoppered flask, a 1:200 p-toluidine-mesitylene mixed solution was placed over **1** (pH 9.62), and the flask was left for two months at room temperature. Yellowish well-developed crystals were formed at the interface between the aqueous and organic phases. When solutions of p-toluidine-mesitylene with ratios between 1:5 and 1:20 were used, the products were not inclusion compounds but a coordination complex of p-toluidine. When this coordination complex was heated at *ca.*450 K, this complex transformed to the inclusion compound, *catena*-[*catena*-(α,ω-Diaminooctane)cadium-μ-tetracyanonickelate]-p-toluidine.[12]

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-o-xylene

In a stoppered flask, a 1:1 o-xylene-mesitylene mixed solution was placed over **1** (pH 9.32), and the flask was left for one month at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-m-xylene

In a stoppered flask, neat m-xylene was placed over **1** (pH 9.32), and the flask was left for one month at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-p-xylene

In a stoppered flask, neat p-xylene was placed over **1** (pH 10.0), and the flask was left for one month at 278 K. Yellowish fine plate-shaped crystals were formed at the interface between the aqueous and organic phases. We have not confirmed the components of this compound.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-o-dichlorobenzene

A 1:5 mixture of o-dichlorobenzene-mesitylene was placed over **1** (pH 9.32) in a stoppered flask, which was left for one month at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-m-dichlorobenzene

Neat m-dichlorobenzene was placed under **1** (pH 9.71) in a stoppered flask, which was left for one month at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-p-dichlorobenzene

A 1:5 mixed solution of p-dichlorobenzene-n-hexane was placed over **1** (pH 9.71) in a stoppered flask, which was left for one month at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and organic phases. We have not confirmed the components of this compound.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-o-nitrotoluene

Neat o-nitrotoluene was placed under **1** (pH 9.62) in a stoppered flask, which was left for one month at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and the organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-2,3-xylidine

Neat 2,3-xylidine was placed under **1** (pH 9.62) in a stoppered flask, which was left for one month at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-2,4-xylidine

A 1:5 2,4-xylidine-mesitylene mixed solution was placed under **1** (pH 9.62) in a stoppered flask, which was left for one month at room temperature. Yellowish crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-2,5-xylidine

A 1:5 2,5-xylidine-mesitylene mixed solution was placed under **1** (pH 9.62) in a stoppered flask, which was left for one month at room temperature. Yellowish crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-2,6-xylidine

A 1:20 2,6-xylidine-n-hexane mixed solution was placed under **1** (pH 9.62) in a stoppered flask, which was left for one month at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-3,4-xylidine

A 1:20 3,4-xylidine-n-hexylalcohol mixed solution was placed under **1** (pH 9.62) in a stoppered flask, which was left for one month at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-3,5-xylidine

A 1:20 3,5-xylidine-n-hexane mixed solution was placed under **1** (pH 9.62) in a stoppered flask, which was left for one month at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-hemimellitene (1,2,3-trimethylbenzene)

Neat hemimellitene was placed over **1** (pH 9.62) in a stoppered flask, which was left for one month at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-*pseudo*cumene (1,2,4-trimethylbenzene)

Neat *pseudo*cumene was placed over **1** (pH 9.62) in a stoppered flask, which was left for one month at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-2,4,6-trimethyaniline

A 1:10 2,4,6-trimethylaniline-mesitylene mixed solution was placed over **1** (pH 9.62) in a stoppered flask, which was left for one month at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-durene (1,2,4,5-tetramethybenzene)

An organic solution of durene in n-hexane (1:20) was placed over **1** (pH 9.62) in a stoppered flask, which was left for one month at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-indene

A 1:20 mixture of indene in n-hexane was placed over **1** (pH 9.62) in a stoppered flask, which was left for one month at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-naphthalene

A 1:20 mixture of naphthalene in n-hexane was placed over **1** (pH 9.62) in a stoppered flask, which was left for one month at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and organic phases. We have not confirmed the components of this compound.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-phenanthrene

A 1:20 mixtue of phenanthroline in n-hexane was placed over **1** (pH 9.62) in a stoppered flask, which was left for one month at 278 K. Yellowish fine crystals were formed at the interface between the aqueous and the organic phases. We have not confirmed the components of this compound.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-pyrrole

A 1:20 mixture of pyrrole and n-hexane was placed over **1** (pH 9.62) in a stoppered flask, which was left for one month at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and the organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-furan

Neat furane was placd over **1** (pH 9.62) in a stoppered flask, which was left for one month at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-thiophene

Neat thiophene was placed over **1** (pH 9.62) in a stoppered flask, which was left for one month at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-benzene

Neat benzene was placed over **1** (pH 9.71) in a stoppered flask, which was left for one month at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and the organic phases. We have not confirmed the components of this compound.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-p-dibromobenzene

A 1:3 mixture of p-dibromobenzene and mesitylene was placed over **1** (pH 9.62) in a stoppered flask, which was left for one month at room temperature. Yellowish fine crystals were formed at the interface between the aqueous and organic phases.

RESULTS

In the following, the coefficient x represents the number of guest molecule per formal unit of the host metal complex in the proposed formula $Cd[NH_2(CH_2)_6NH_2]\ Ni(CN)_4 \cdot x$Guest.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-fluorobenzene

Anal. Calcd for x = 1.0(%) : C, 39.42; H, 4.34; N, 17.24. Found: C, 39.22, H, 4.41; N, 17.42.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-chlorobenzene

Anal. Calcd for x = 1.0 (%): C, 38.13; H, 4.20; N, 16.68. Found: C, 37.92, H, 4.15; N, 16.51.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-bromobenzene

Anal. Calcd for x = 1.0(%): C, 35.04; H, 3.85; N, 15.32. Found: C, 34.97, H, 4.03; N, 15.43.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-iodobenzene

Anal. Calcd for x = 1.0(%): C, 32.38; H, 3.56; N, 14.12. Found: C, 32.38, H, 3.51; N, 13.82.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-toluene

Anal. Calcd for x = 1.0(%): C, 42.22; H, 5.00; N, 17.38; Cd, 23.24; Ni, 12.14. Found: C, 41.81, H, 4.81; N, 17.34; Cd, 23.54; Ni, 12.05.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-aniline

Anal. Calcd for x = 1.0(%): C, 39.66; H, 4.78; N, 20.24. Found: C, 39.37, H, 4.67; N, 19.98.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-phenol

Anal. Calcd for x = 1.0(%): C, 39.38; H, 4.57; N, 17.31. Found: C, 39.45, H, 4.52; N, 17.13.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-nitrobenzene

Anal. Calcd for x = 0.5(%): C, 35.09; H, 4.19; N, 20.46. Found: C, 35.61, H, 4.18; N, 18.79. We have not confirmed the components of this compound.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-ethylbenzene

Anal. Calcd for x = 0.7(%): C, 40.23; H, 4.98; N, 18.04. Found: C, 40.21, H, 4.96; N, 17.54.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-styrene

Anal. Calcd for x = 0.9(%): C, 42.58; H, 4.82; N, 17.32. Found: C, 42.33, H, 4.97; N, 17.05.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-phenylacetylene

Anal. Calcd for x = 1.0(%): C, 43.81; H, 4.49; N, 17.29. Found: C, 43.91, H, 4.46; N, 16.81.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-N,N-dimethylaniline

Anal. Calcd for x = 0.8(%): C, 40.33; H, 4.83; N, 19.08. Found: C, 40.20, H, 4.83; N, 19.08.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-o-toluidine

Anal. Calcd for x = 1.0(%): C, 40.95; H, 5.05; N, 19.66. Found: C, 40.57, H, 4.86; N, 19.69.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-m-toluidine

Anal. Calcd for x = 1.0(%): C, 40.95, H, 5.05; N, 19.66. Found: C, 40.73, H, 5.15; N, 19.57.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-p-toluidine

Anal. Calcd for x = 0.9(%): C, 40.13; H, 4.98; N, 19.81; Cd, 23.04; Ni, 12.03. Found: C, 39.13, H, 5.00; N, 19.07; Cd, 22.79; Ni, 12.12.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-p-toluidine (thermal decomposition compound)

Anal. Calcd for x = 0.7(%): C, 38.37; H, 4.81; N, 20.12. Found: C, 38.90, H, 5.07; N, 19.23.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-o-xylene

Anal. Calcd for x = 0.9(%): C, 42.4; H, 5.2; N, 17.3. Found: C, 42.06, H, 4.85; N, 16.66.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-m-xylene

Anal. Calcd for x = 0.75(%): C, 40.8; H, 5.1; N, 17.8. Found: C, 40.91, H, 5.33; N, 17.37.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-p-xylene

Anal. Calcd for x = 0.7(%): C, 40.2; H, 5.0; N, 18.0. Found: C, 38.14, H, 4.89; N, 16.80. We have not confirmed the components of this compound as mentioned previously.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-o-dichlorobenzene

Anal. Calcd for x = 1.0(%): C, 35.69; H, 3.74; N, 15.61. Found: C, 35.56, H, 3.64; N, 15.80.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-m-dichlorobenzene

Anal. Calcd for x = 0.75(%): C, 34.72, H, 3.82; N, 16.75. Found: C, 34.46, H, 3.70; N, 16.21.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-p-dichlorobenzene

Anal. Calcd for x = 0.77(%): C, 34.82; H, 3.80; N, 16.62; Cd, 22.28; Ni, 11.63. Found: C, 37.37, H, 4.33; N, 16.54; Cd, 22.23; Ni, 11.61. We have not confirmed the components of this compound as mentioned previously.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-o-nitrotoluene

Anal. Calcd for $x = 0.85$(%): C, 37.71; H, 4.36; N, 18.89. Found: C, 37.38, H, 4.46; N, 18.61.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-2,3-xylidine

Anal. Calcd for $x = 1.0$(%): C, 42.18; H, 5.31; N, 19.13. Found: C, 41.78, H, 5.31; N, 19.13.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-2,4-xylidine

Anal. Calcd for $x = 0.75$(%): C, 39.84; H, 5.06; N, 19.60. Found: C, 39.07, H, 5.11; N, 19.10.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-2,5-xylidine

Anal. Calcd for $x = 1.0$(%): C, 42.18; H, 5.31; N, 19.13. Found: C, 41.62, H, 5.36; N, 18.95.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-2,6-xylidine

Anal. Calcd for $x = 0.7$(%): c, 39.34; H, 5.01; N, 19.70. Found: C, 39.24, H, 5.26; N, 19.43.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-3,4-xylidine

Anal. Calcd for $x = 0.6$(%): C, 38.30; H, 4.91; N, 19.92. Found: C, 38.32, H, 5.16; N, 18.63. We have not confirmed the components of this compound.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-3,5-xylidine

Anal. Calcd for $x = 0.75$(%): C, 39.84; H, 5.06; N, 19.60. Found: C, 40.43, H, 5.48; N, 19.20.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-hemimellitene (1,2,3-trimethylbenzene)

Anal. Calcd for $x = 0.9$(%): C, 43.51; H, 5.40; N, 16.82. Found: C, 43.57, H, 5.16; N, 16.60.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-*pseudo*cumene (1,2,4-trimethylbenzene)

Anal. Calcd for $x = 0.7$(%): C, 41.17; H, 5.17; N, 17.68. Found: C, 40.69, H, 5.73; N, 16.83. We have not confirmed the components of this compound precisely.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-2,4,6-trimethyaniline

Anal. Calcd for $x = 1.0$(%): C, 43.33; H, 5.55; N, 18.61. Found: C, 43.68, H, 5.57; N, 17.95.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-durene (1,2,4,5-tetramethybenzene)

Anal. Calcd for $x = 0.7$(%): C, 42.07; H, 5.35; N, 17.31. Found: C, 41.61, H, 4.94; N, 16.72.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-indene

Anal. Calcd for $x = 1.0$(%): C, 44.96; H, 4.77; N, 16.56. Found: C, 45.16, H, 4.70; N, 16.37.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-naphthalene

No satisfactory samples were prepared.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-phenanthrene

Anal. Calcd for $x = 2.2$(%): C, 62.54; H, 4.89; N, 10.73. Found: C, 62.45, H, 5.00; N, 6.22. We have not confirmed the components of this compound as mentioned previously.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-pyrrole

Anal. Calcd for $x = 0.9$(%): C, 36.16; H, 4.57; N, 21.39. Found: C, 35.91, H, 4.44; N, 20.89.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-furan

Anal. Calcd for $x = 0.85$(%): C, 35.83; H, 4.35; N, 18.71. Found: C, 35.66, H, 4.37; N, 18.31.

catena-[*catena*-(α,ω)-Diaminooctane)cadmium-μ-tetracyanonickelate]-thiophene

Anal. Calcd for $x = 0.9$(%): C, 35.11; H, 4.25; N, 18.06. Found: C, 34.80, H, 4.24; N, 17.84.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-benzene

Anal. Calcd for x = 0.5(%): C, 36.27; H, 4.45; N, 19.52; Cd, 26.11; Ni, 13.64. Calcd for x = 1.0(%): C, 40.93; H, 4.72; N, 17.90; Cd, 23.94; Ni, 12.50. Found: C, 36.15, H, 4.80; N, 14.88; Cd, 23.23; Ni, 12.10. We have not confirmed the components of this compound as mentioned previously.

catena-[*catena*-(α,ω-Diaminooctane)cadmium-μ-tetracyanonickelate]-p-dibromobenzene

Found: C, 5.71, H, 4.29; N, 15.15%. We could not analyze the data.

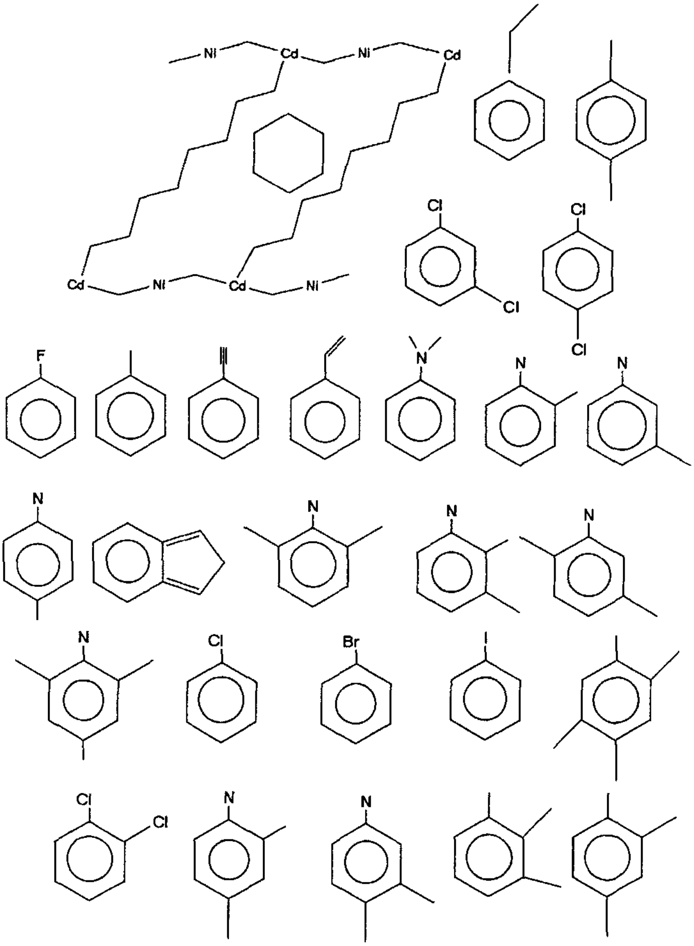

Figure 1 A typical "all-*trans*" *catena*-[*catena*-(α,ω-diaminohexane)cadmium-μ-tetracyanonickelate] host structure and representative guest molecules.

DISCUSSION

When diaminohexane was added to an aqueous solution containing $CdCl_2 \cdot 2.5H_2O$ and $K_2[Ni(CN)_4]$, a turbidity was formed. The turbidity disappeared upon addition of citric acid and monoethanolamine, which acted as complementary complexing agents for cadmium(II). After the aqueous solution was filtered through a plastic membrane filter, it was covered with an organic phase of the guest species to be accommodated. The concentration of the metal species was kept at about 0.1 mol dm^{-3} in the final aqueous solution. The organic phase used was the neat liquid of the guest species or the mixture of the guest species and organic diluents such as mesitylene and n-hexane. The resulting compounds were obtained in several forms: well developed crystals, fine crystals, plate-like crystals, or massive crops.

There are many conditions to be considered for the preparation procedure. Among them: (i) concentration of diamines, (ii) the kind and amount of complementary complexing agents to adjust the pH, (iii) diluents of guest molecules, and (iv) temperatures.

When the amount of diamine is less than twice the molar amount of the metal species, the turbidity once formed hardly disappeared by adding even excessive complementary complexing reagents. The appropriate value of pH in the aqueous solution depends on the diamine and guest applied. For example, in the case of o-toluidine, the values had been checked from 8.6 to 10.45 until the most appropriate value 10.2 was found. For the 2,4-xylidine compound of the same host, the value was 10.0.

The guest species holding the solid state at ambient temperature were dissolved in mesitylene or n-hexane, which were not included as guest species in the diaminohexane host. Ethylbenzene was not used as a solvent beause it could be accommodated in the diaminohexane host.

The effect of temperature was studied at room temperature (*ca.* 293 K) and at *ca.* 273 K in a refrigerator for a number of compounds with no affect on formation of crystals. This is a remarkable contrast to other Hofmann-type clathrates which usually give well developed crystals at lower temperatures.

Most complexes reported here have a value of $x = 0.7 \sim 1.0$ in the general formula of $Cd[NH_2(CH_2)_6NH_2]Ni(CN)_4.\chi Guest$. The single X-ray crystallography studies of toluidines and xylenes show a compartment structure with the diaminohexanes in an all-*trans* arrangement.[1-4] The diaminohexane, which has even numbered carbon chain, has an advantage in forming this stable structure compared to other diamines with odd number ones. Although most give a guest/host ratio of about one suggesting that they are isostructural, a number of compounds show rather non-stoichiometric compositions with regard to the number of guest molecules per formula unit of the metal complex host. This is obviously because of defects of guest molecules in the crystals, but in order to elucidate the inclusion structures in detail, a crystal structure determination is essential for each compound.

It is notable that the guest molecules having an amino group as the substitute group on the aromatic ring are better for accommodating a host than those guests which are comparable in size and shape but lacking amino groups. This can be attributed to the size of an amino group which is relatively smaller than a methyl group and suitable for the host cavity. The polarity of an amino group may also contribute to formation of inclusion compounds. Further study in this line is now underway.

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