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Autoreduction of Pd–Co and Pt–Co Cyanogels: Exploration of Cyanometalate Coordination Chemistry at Elevated Temperatures

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Abstract: Cyanogels are coordination polymers made from the reaction of a chlorometalate and a cyanometalate in aqueous solution, which undergo a sol–gel transition to form stable gels. At temperatures above 240 °C, the cyanide ligand acts as a reducing agent and reduces the metal centers to lower oxidation states. To understand the mechanism of the autoreduction, the thermal reduction of the Pd–Co cyanogel system formed by the reaction of $PdCl_4^{2-}$ and $Co(CN)_6^{3-}$ was studied in an inert atmosphere. It was found that the reduction proceeds through two polymeric cyanide-containing intermediates, $CoPd(CN)_4$ and $Pd(CN)_2$, that form upon reduction of Co^{3+} to Co^{2+} and involves a significant rearrangement of the coordination structure. The two intermediates upon further heating reduce to metallic products, which by solid-state diffusion form a single Pd/Co alloy product. $CoPd(CN)_4$ was found to have a hydrated form $Co(H_2O)_2Pd(CN)_4 \cdot 4H_2O$ with a layered structure crystallizing in an orthorhombic *Pnma* space group. The Pt–Co cyanogel was found to autoreduce via a similar route. $CoPt(CN)_4$ was confirmed as an intermediate. Understanding of the mechanism of the cyanogel autoreduction is an important step toward better understanding of opportunities that cyanogels offer in materials chemistry, as well as an expansion of the knowledge of coordination chemistry at elevated temperatures in general.

Introduction

Cyanometalate chemistry has recently experienced a renaissance particularly owing to remarkable magnetic,[1–4] electrical,[5] optical,[6] and catalytic[7] properties, as well as gas-storage capabilities,[8–10] of some one-, two-, and three-dimensional extended systems of single- and double-metal cyanides with bridging cyanide ligands. Cyanogels, coordination polymers made from a mixture of a chlorometalate and a cyanometalate in aqueous solution,[11–13] are a special class of three-dimensional double-metal cyanides; unlike other three-dimensional cyano-

metalate-based materials, cyanogels do not form crystalline or metastable gel-like precipitates. Instead, they undergo a true sol–gel transition to form stable gels, which upon drying have a well-defined micro- and mesoporosity.[10] Simple cyanometalates and related polynuclear transition-metal cyanides are known to thermally decompose to various transition-metal species and gaseous products.[14–17] In contrast, cyanogels upon traditional heating or upon microwave irradiation autoreduce to transition-metal alloys and transition-metal salts with the concomitant formation of cyanogen gas.[11,13,18,19] Because of this autoreduction chemistry, cyanogels are excellent precursors for transition-metal alloys.[13] In addition, taking advantage of the sol–gel transition has allowed for the preparation of supported transition-metal alloy nanoparticles[20] and nanoparticle thin films,[20–22] while the porous morphology along with the

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intrinsic presence of alkali salts has been found to promote the formation of ultrafine pore cellular metals.[11,18]

The thermolysis of the 2:1 $K_2PdCl_4/K_3Co(CN)_6$ cyanogel has been studied previously.[11,18] This cyanogel was found to start decomposing below 250 °C and reduce to a Pd/Co alloy. This makes it chemically distinct from its cyanometalate precursor, $K_3Co(CN)_6$, which has been reported to start decomposing at 420 °C,[15,23] forming a variety of products including KCN and Co_3C. Similar lowering of the decomposition temperature when compared to the parent compound $K_3Co(CN)_6$ was observed in coordination polymers $KM^{II}Co(CN)_6 \cdot xH_2O$ (M = Mn, Fe, Co, Ni, Cu, and Zn) and was explained by decreased crystallinity of the polymer with respect to the parent compound.[17] However, as observed for $K_3Co(CN)_6$ many of these coordination polymers were reported to decompose into metal carbides. The cyanogel decomposition pattern appears to be more similar to that reported for platinum cyanometalates, which decompose to pure platinum metal and simple salts with the concomitant evolution of cyanogen.[16]

Previous work suggested that autoreduction of cyanogels to alloys may not be direct but may involve several intermediates.[11,13] Indeed, the current work shows that thermal decomposition of the 2:1 $Na_2PdCl_4/K_3Co(CN)_6$ cyanogel occurs via a significant rearrangement leading to polymeric double- and single-metal cyanides, containing Pd^{2+} and Co^{2+} centers. These intermediates upon further heating autoreduce to metals, eventually forming a single alloy product by solid-state diffusion. Understanding the autoreduction chemistry is important not only with respect to the chemical nature and composition of the final product but may also help in understanding the processes that drive the formation of the porous morphology observed under some preparation conditions.[11] In the broader context, the autoreduction chemistry of cyanogels is part of the elevated temperature chemistry of cyanometalates, which possesses some intriguing features but has not been studied in great detail. Cyanide at room temperature is a weak reducing agent $[(CN)_2(g)/HCN = 0.37$ V versus SHE,[24] but at elevated temperatures, it is capable of reducing metals to lower oxidation states.[11,16,17,25] This reduction is sometimes complete, leading to metal and cyanogen gas,[11,16,17] but in many cases, cyanide bond cleavage is observed, producing metal carbides, carbon, and nitrogen.[15,17,25] Whether a redox process occurs is reasonably related to the reduction potential of the transition metals involved. However, because redox potentials for both the cyanogen/cyanide couple and the metals of interest are not readily available at temperatures pertinent to this study, this statement cannot be analytically tested.

It has been previously reported that an increased temperature can lead to "cyanide flipping" in the bridged complexes,[14,25–27] and this may play a role in the reduction processes. It has also been observed that the temperature of reduction is affected by the chemical environment of the cyanide; bridging cyanide ligands reduce metal centers at lower temperatures than the corresponding terminal cyanides.[11,17] The above-mentioned features of the cyanometalate chemistry imply that the coordina-

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Chart 1. Heating and Washing Processes in the Separation of Intermediates of the Pd–Co Cyanogel Autoreduction
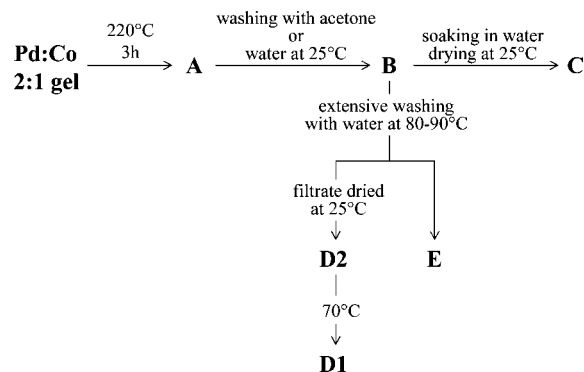
tion chemistry of cyanide-containing compounds at elevated temperature is quite distinctive from the relatively well-understood chemistry of these compounds at room temperature. The study of cyanometalates and related compounds, such as cyanogels, at elevated temperatures expands known coordination chemistry into a new realm.

To elucidate the autoreduction chemistry of cyanogels, we first monitored the progress of the autoreduction reaction of the 2:1 $Na_2PdCl_4/K_3Co(CN)_6$ cyanogel thermally induced by microwave irradiation via analyses of samples of the same cyanogel irradiated for increasing amounts of time. Given this information, the standard thermally induced decomposition was evaluated and found to proceed via an identical reaction pathway. The intermediate stage in the conversion of the Pd–Co and Pt–Co cyanogels to metal was investigated, and the intermediates of the reaction in the Pd–Co system were isolated and characterized. The experimental data presented in this paper, along with results published previously,[11] provide a fairly complete picture of the thermal decomposition pathway.

Experimental Section

Materials. Na_2PdCl_4 was purchased from Pressure Chemical Co. $K_3Co(CN)_6$, $CoCl_2$, and NH_4OH were purchased from Aldrich. $K_2Pd(CN)_4$ and $Pd(CN)_2$ were purchased from Alfa Aesar. Acetone and ethanol were solvent-grade.

Gel Preparation. Pd–Co gel was prepared by mixing 60 mM Na_2PdCl_4 and 60 mM $K_3Co(CN)_6$ in a 2:1 volume ratio. The gel was aged for 1–2 days, filtered to remove water, and dried at 25 °C. After drying, it was crushed to a fine powder, washed with water, and dried again. The Pt–Co gel was made from 100 mM solutions of K_2PtCl_4 and $K_3Co(CN)_6$ mixed in a 2:1 volume ratio and heated at 95 °C for 1 day. A number of products were made from the 2:1 Pd/Co gel by various types of heating, washing, and soaking. These treatments are schematically summarized in Chart 1.

Thermal Processing. Thermal processing was performed in a three-zone programmable 2416 cm³ Carbolite furnace with a 12 °C/min ramp under flowing argon using a flow rate of approximately 60 mL/min. To monitor the reaction progress of the conversion of Pd–Co cyanogel to alloy under a static inert atmosphere, several samples of the same cyanogel under argon were irradiated with the full power of a 1100 W SHARP R-305HW domestic microwave oven for various time periods between 10 and 240 s. The details of the setup were described elsewhere.[13,19] After cooling, the tube was opened and the solid products of the reaction were analyzed by infrared (IR) and X-ray diffraction (XRD). The products were washed with acetone, ethanol, or water, and the filtrates were analyzed by UV–vis. **Warning**: During heating, hazardous gases, $(CN)_2$ and HCN, are evolved. A series of two bubblers was used to trap the evolved gases. The first one contained

a solution of bleach, and the second one contained a 1 M aqueous solution of NaOH.

Crystal Growth. A 25 mM aqueous solution of $K_2Pd(CN)_4 \cdot 3H_2O$ was placed in a screw-cap vial, followed by an equal layer of a 1:1 volume mixture of ethanol and water and a top layer of 25 mM $CoCl_2$ in ethanol. The vial was allowed to sit for 3 weeks, after which pink prisms formed on the walls of the vial in the middle layer. Crystals for the powder pattern of the blue compound were made by drying the pink crystals and heating them at 220 °C for 3 days under argon to ensure complete dehydration and enhance the quality of crystals.

Analyses. Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Nicolet 730 FTIR spectrometer using KBr pellets and on a Thermo-Nicolet 6700 FTIR equipped with a Smart Orbit diamond ATR attachment. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 with a 1 or 5° min^{-1} ramp rate. The same set of traps as in the furnace heating was used in the TGA to avoid cyanogen release. UV–vis spectra were recorded on a HP 8453 diode array spectrophotometer using quartz cuvettes. Inductively coupled plasma (ICP) was performed on Perkin-Elmer Optical Emission Spectrometer Optima 4300 DV. Mass spectrometry analysis was performed on a Hewlett-Packard 5989B (Electrospray) MS Engine. XPS analysis was performed with the aid of a Phoibos 150 hemispherical energy analyzer (SPECS) and a monochromatic Al source (1486.6 eV) using powdered samples mounted on a piece of carbon tape. The spectrometer was calibrated to the position of the $3d_{5/2}$ line of sputter-cleaned Ag at a binding energy of 368.25 eV and the C1s line of HOPG at 284.5 eV. Scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) analysis was performed on a FEI XL30 FEG-SEM equipped with a PGT-IMIX PTS EDX system using a 15 keV electron beam. The samples were coated with 3–5 nm of iridium to increase conductivity using a VCR IBS/TM250 ion-beam sputterer.

X-ray Diffraction. Single-crystal X-ray data were collected using a Nonius KappaCCD diffractometer equipped with a MSC X-stream cryosystem and Mo Kα ($\lambda = 0.710\ 73$ Å) radiation at 200 K. Initial atomic positions were taken from the previously reported $Co(H_2O)_2Ni(CN)_4 \cdot 4H_2O$ structure[28] and refined using SHELXTL.[29] Also nonhydrogen atoms were refined anisotropically. The hydrogen atoms, which were disordered over multiple sites, were located in difference Fourier maps and assigned isotropic displacement coefficients $U(H) = 1.5U(O)$. Powder X-ray data were collected on a Bruker D8 Focus in a Bragg–Brentano geometry with a Cu Kα source ($\lambda = 1.540\ 51/1.544\ 33$ Å), a graphite diffracted beam monochromator, and a scintillation counter.

Results

TGA data showing four mass losses during the thermolysis of the 2:1 Pd/Co gel are shown in Figure 1 and were also published previously along with DSC data.[11] The first mass loss (1) is completed by 100 °C and is due to the loss of residual water from the xerogel as shown by the evolved gas analysis.[11] The second mass loss (2) is observed around 200 °C, and the third mass loss (3) is observed around 390 °C; both were associated with the evolution of $(CN)_2$ and a trace amount of HCN detected by mass spectrometry.[11] The last mass loss (4) begins around 650 °C and is explained by sublimation of alkali salts (NaCl and KCl), which are byproducts of both the polymerization and the autoreduction. The two successive losses of CN ligands suggest that the autoreduction reaction consists of at least two major processes and that one or more cyanide-containing intermediates exist between the two $(CN)_2$ evolution
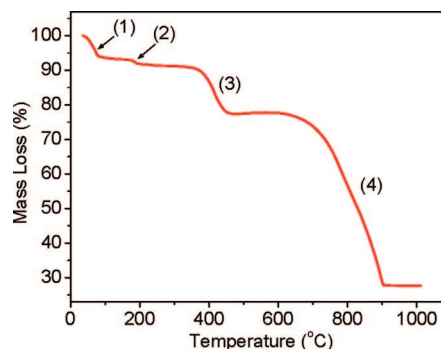
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Figure 1. TGA of the 2:1 Pd/Co cyanogel under argon with a 5 °C min^{-1} ramp rate.

steps. The major portion of this work focused on isolating and identifying these intermediates and observing their appearance and disappearance during the progress of the reaction. Because the end product of the autoreduction of the Pd/Co cyanogel is an alloy, the emergence and disappearance of the metallic intermediates was also monitored.

We have previously reported that Pd–Co cyanogel autoreduction can be achieved by microwave irradiation with the same outcome as in the furnace but on a much shorter time scale.[19] The similarities between IR spectra of intermediate stages of the autoreduction reaction effected by microwave irradiation and the IR spectra of different stages of the reaction in the furnace recorded previously[11,30] suggest that both microwave irradiation and furnace heating can be used to monitor the reaction progress. In this work, the reaction progress in the Pd–Co cyanogel-to-alloy conversion was monitored by analyzing samples of the same gel irradiated by microwaves for increasing amounts of time. IR spectra of these samples are shown in Figure 2, and XRD patterns are shown in Figure 3. Furnace heating was used to prepare large amounts of the intermediate present between the two CN losses to allow for separation and identification of the components of this intermediate (Chart 1 and Table 1).

The native gel was orange and exhibited a bridging and terminal CN stretch in the IR, at 2196 and 2146 cm^{-1}, as assigned previously.[11] The gels irradiated by microwaves for 10 and 15 s were also orange and exhibited only broadening of the CN peaks. Between 15 and 20 s into the reaction rapid evolution of a gas was observed. Mass spectrometry allowed for the identification of the gas as cyanogen.[11,19] At 20 s, blue color appeared in the sample (intermediate **A**) and IR showed very significant changes (Figure 2): a new peak at 2192 cm^{-1} and a number of new peaks at higher frequency (2211, 2225, and 2235 cm^{-1}), all most likely corresponding to bridging cyanides. The original terminal CN peak at 2146 cm^{-1} disappeared and was replaced by a weaker peak at a slightly higher frequency of 2152 cm^{-1}. In the low-frequency region, the 503 cm^{-1} peak assigned to Co–C stretching[11] in the native Pd–Co cyanogel became smaller and two new peaks at 453 and 535 cm^{-1}, respectively, appeared. When the 20 s sample was washed with acetone, the UV–vis spectra of the filtrate contained features of Co^{2+} complexes with Cl$^-$ and acetone,[31] suggesting the presence of $CoCl_2$ in the product. In XRD (Figure 3), peaks for alkali chlorides (NaCl and KCl) appeared in the pattern along

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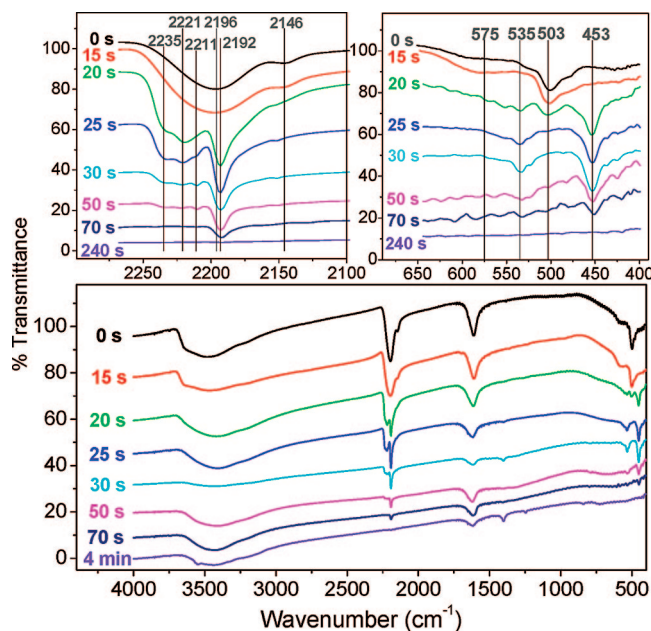(31) Stanescu, G.; Trutia, A. *J. Optoelectron. Adv. Mater.* **2005**, *7*, 1009–1015.

Figure 2. IR spectra of Pd−Co cyanogel at various times of microwave irradiation (bottom). The cyanide region is enlarged at the top left, and the low frequency region is enlarged at the top right. The peaks around 3500 and 1600 cm^{-1} are characteristic of water.

with poorly defined broad peaks at low angles, which are most likely characteristic of components of the blue intermediate.

The first CN loss from the gel leading to the formation of a blue product **A** was studied by TGA (Figure 4) of a washed gel. Using a washed gel ensured that the mass after dehydration in the TGA was attributable entirely to the polymer network and not to alkali salts, which are byproducts of polymerization. The TGA showed a mass loss of 3.9% between 140 and 250 °C, corresponding to the loss of one CN ligand per Co center in the polymer.

XRD analysis of **A** prepared in the furnace by heating a gel at 220 °C for 3 h indicated that **A** contained NaCl and KCl, consistent with the observations from microwave experiments. Further experiments showed that **A** also contained CoCl$_2$ and two cyanide-containing compounds **D** and **E**, as discussed below. When the blue material **A** was placed in acetone or ethanol, the solvent immediately turned blue but most of the compound did not dissolve. The UV–vis spectra of the acetone filtrate contained features of Co^{2+} complexes with Cl$^-$ and acetone,[31] and the XRD of the dried filtrate corresponded to the XRD of the hydrated form of CoCl$_2$ uniquely identifying CoCl$_2$ as a component of **A**. Acetone was used to completely extract the CoCl$_2$ from the sample. The remaining solid was blue (**B**). The IR of **B** (Figure 5) was the same as that of **A** and contained the same features as that of the sample irradiated by microwaves for 20 s (Figure 2). XPS spectra of the blue intermediate **B** and the Pd−Co gel indicated that the binding energies for the Pd 3d$_{5/2}$ and 3d$_{3/2}$ electrons, respectively, were the same in the gel and in the blue intermediate (341.6 and 346.8 eV), indicating that the oxidation state of Pd in the gel and in **B** was the same, Pd^{II}. When **B** was placed in water, it changed color to pinkish beige (**C**) over a period of 2 days and colored the solvent faint pink. The CN region of the IR spectrum of **C** dried at 25 °C was very similar to the IR of **B**, except for the 2192 cm^{-1} peak, which was replaced by a peak at 2176 cm^{-1} (Figure 5). When **C** was dried at 70 °C, its color changed back to blue and the IR again became that of **B**. When two
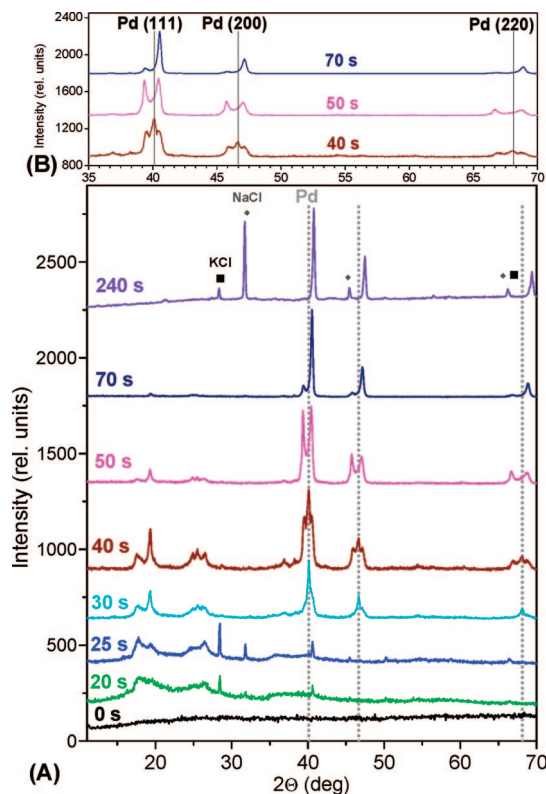

Figure 3. (A) XRD spectra of Pd−Co cyanogel at various stages of microwave irradiation. Samples irradiated for 30–70 s were washed to remove salts before XRD measurements. In the 240 s sample, NaCl was used as an internal standard. (B) Closer view of the FCC phases present between 40 and 70 s of irradiation.

samples of the light pink filtrate from the washing of **B** with water were dried, one at 70 °C and the other at 25 °C, two differently colored materials were obtained. Drying at 70 °C produced a blue powder (**D1**), while drying at 25 °C produced a pink powder (**D2**). The IR spectra of the blue and pink sample contained one weak but sharp peak at 2192 and 2177 cm^{-1}, respectively. The low wavenumber region of the blue material contained peaks at 534 and 451 cm^{-1} with shoulders at 524 and 439 cm^{-1}, while the pink material exhibited one peak at 427 cm^{-1}.

To isolate **D** from **A** in large quantities, **A** was first washed with water until no precipitate was detected with AgNO$_3$ to make sure no CoCl$_2$ and alkali salts remained (some **D** was lost in the process because of some solubility in water). The remaining material was washed several times in water at 80–90 °C and then filtered, producing **E**. Pink solid **D2** and blue solid **D1** were obtained by drying the filtrate at 25 and 75 °C, respectively. IR of **D1**, **D2**, and **E** is shown in Figure 6. IR of **E** dried at room temperature showed two strong CN peaks at 2220 and 2235 cm^{-1}, a shoulder at 2152 cm^{-1}, and two relatively strong peaks at 550 and 462 cm^{-1}. Some asymmetric broadening around 2180–2190 cm^{-1} was observed, most likely because of residual **D** in the sample. **E** was identified as Pd(CN)$_2$ because of similarities in IR between **E** and Pd(CN)$_2$. The IR of commercially available Pd(CN)$_2$ contains a broad feature in the CN region, with a maximum absorption at 2215 cm^{-1} and two shoulders around 2150 cm^{-1}. In the literature, Pd(CN)$_2$ was reported to exhibit a CN stretch[32] at 2220 cm^{-1}, and although its structure is not known, it has been suggested that it is a coordination polymer with sheets of Pd atoms bridged by CN ligands.[33] The low-frequency spectrum of the commercially

Table 1. Preparation, IR Features, and Identified Components of Intermediates

product	preparation	IR peaks	components
A	2:1 Pd/Co gel heated at 220 °C for 3 h	CN: 2235, 2221, 2192, 2152 (s) low $\bar{\nu}$: 553, 536, 524 (s), 455, 439 (s)	CoPd(CN)$_4$, Pd(CN)$_2$, CoCl$_2$, KCl, NaCl
B	**A** extensively washed with acetone or washed with water at 25 °C	CN: 2235, 2221, 2192, 2152 (s) low $\bar{\nu}$: 553, 536, 524 (s), 455, 439 (s)	CoPd(CN)$_4$, Pd(CN)$_2$
C	**B** after soaking in water and dried at 25 °C	CN: 2235, 2221, 2176, 2152 (s) low $\bar{\nu}$: 550, 462, 427 H$_2$O: 3625, 3565	Co(H$_2$O)$_2$Pd(CN)$_4$·4H$_2$O, Pd(CN)$_2$
D1	filtrate from **B** soaked in water at 80–90 °C and dried at 70 °C	CN: 2192, 2152 (s) low $\bar{\nu}$: 534, 524 (s), 451, 439 (s)	CoPd(CN)$_4$
D2	filtrate from **B** soaked in water at 80–90 °C and dried at 25 °C	CN: 2177, 2152 (s) low $\bar{\nu}$: 427 H$_2$O: 3618, 3559	Co(H$_2$O)$_2$Pd(CN)$_4$·4H$_2$O
E	**A** or **B** extensively washed with water	CN: 2235, 2220 low $\bar{\nu}$: 550, 462	Pd(CN)$_2$

available Pd(CN)$_2$ contained peaks at 548 and 463 cm^{-1}, similar to **E** within experimental error.

Dehydrated blue material **D1** exhibited a CN peak at 2192 cm^{-1}, a shoulder at 2150 cm^{-1}, and two peaks in the low-wavenumber region at 534 and 451 cm^{-1}. The hydrated pink form (**D2**) had the CN peak shifted to 2177 cm^{-1}; in the low wavenumber region, a strong sharp peak occurred at 427 cm^{-1}. In addition, two peaks appeared at 3618 and 3559 cm^{-1}, which are associated with the H$_2$O ligands. It should be noted that adding IR spectra of anhydrous **D1** and **E** gives the spectra of the original mixture **B** and that the superposition of hydrated **D2** and **E** gives the spectrum of **C** (Figure 5).

ICP analysis of **D** dissolved in water showed a Pd/Co ratio of exactly 1:1. EDX of **D1** showed both Pd and Co, while EDX of the remaining material showed mostly Pd and a very small amount of Co. No clear signal for Na, K, or Cl was detected by EDX in either compound. Because it is very difficult to completely wash out **D** from **B**, it is likely that Co detected by EDX in the remaining material originated from trace amounts of **D**, while **E** actually contains only Pd. By TGA (Figure 7), the total mass loss from **D1** was 38%, which corresponds to the loss of all four cyanides (MW 104) from a compound with stoichiometry PdCo(CN)$_4$ (MW 269). The mass loss in **E** after dehydration was 34%, consistent with the 33% mass decrease expected in the loss of two cyanides (MW 52) from Pd(CN)$_2$ (MW 158).

Magnetization measurements were performed on the blue compound **D1**. The measured magnetic susceptibility (in emu Oe^{-1} g^{-1}) of **D1** as a function of the temperature is shown in Figure 8. When the stoichiometry CoPd(CN)$_4$ is assumed for **D1**, the plot of inverse magnetic susceptibility per formula unit $1/\chi$ (in units Oe mol emu^{-1}) versus T has a slope of 0.582 and
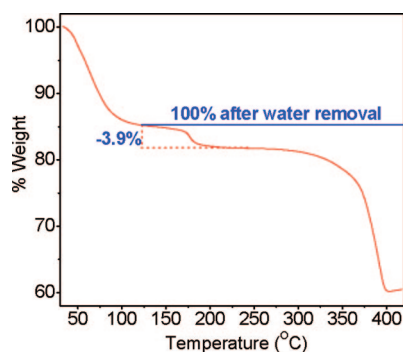
allows one to calculate the Curie constant for **D1** to be $C = 1.718$ and $p_{eff} = 3.71$,[34] which is very close to a value expected for a compound with three unpaired electrons.[35,36]

The solubility of compound **D** in water suggested that its polymeric nature is not maintained in solution. Also, the electrospray mass spectrum of **D** dissolved in water did not contain any high mass peaks, indicating the presence of a polymer, and the only two peaks with the characteristic isotope-splitting pattern of Pd corresponded to the Pd(CN)$_4^{2-}$ species (highest intensity at m/z 105) and the Pd(CN)$_3^-$ species (highest intensity at m/z 184). It was hypothesized that the pink color of **D** in solution is a consequence of the presence of octahedral Co(H$_2$O)$_6^{2+}$ species in solution and that the compound might be a coordination covalent compound CoPd(CN)$_4$, in which the carbon atom of the cyanide ligand is bound to the Pd metal center. It was suggested that the compound could alternatively be formed by reacting Co^{2+} with Pd(CN)$_4^{2-}$. Mixing equimolar aqueous solutions of CoCl$_2$ and K$_2$PdCl$_4$ indeed led to the formation of a pink precipitate, which turned blue when dried on a hot plate. The IR spectra of the two compounds (Figure 9) looked identical to the spectra of hydrated and dehydrated **D** (Figure 6).

Single-crystal diffraction of the pink compound indicated the compound has a formula Co(H$_2$O)$_2$Pd(CN)$_4$·4H$_2$O and crystallizes in an orthorhombic *Pnma* space group with unit cell $a = 12.0861(12)$ Å, $b = 14.1868(15)$ Å, and $c = 7.3728(7)$ Å (see the Supporting Information). This material is isostructural with previously reported orthorhombic Cd(H$_2$O)$_2$Ni(CN)$_4$·4H$_2$O[37] and Co(H$_2$O)$_2$Ni(CN)$_4$·4H$_2$O[28] crystallizing in the *Pnma* space group. The Co(H$_2$O)$_2$Pd(CN)$_4$·4H$_2$O structure was solved in this work and also recently reported by Robertson et al.[7] The structure consists of two-dimensional sheets, in which square planar Pd(CN)$_4$ units are linked through the nitrogen end of the CN ligand to octahedral Co^{2+}. Two water ligands complete the coordination of the Co center, and an additional four water molecules are trapped between the metal—cyanide sheets. Our structure includes a more complete model of hydrogens than

Figure 4. TGA of a 2:1 Pd/Co cyanogel from which alkali salts were removed by washing.

(32) Elsayed, M. F. A.; Sheline, R. K. *J. Inorg. Nucl. Chem.* **1958**, *6*, 187–193.
(33) Dows, D. A.; Haim, A.; Wilmarth, W. K. *J. Inorg. Nucl. Chem.* **1961**, *21*, 33–37.
(34) Morrish, A. H. *The Physical Principles of Magnetism*; R. E. Krieger Pub. Co.: Huntington, NY, 1980.
(35) Ashcroft, N. W. *Solid State Physics*; Holt, Rinehart and Winston: New York, 1976.
(36) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins College Publishers: New York, 1993.
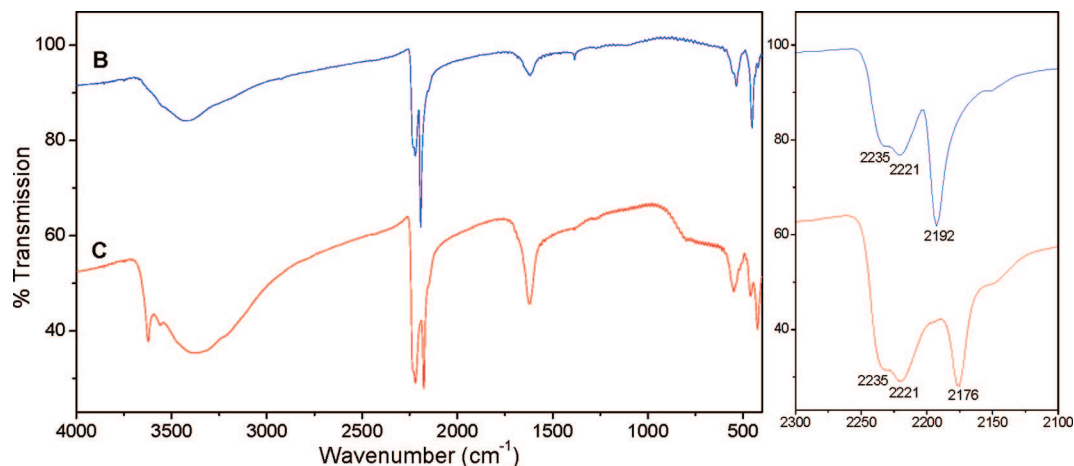
Figure 5. IR spectra of **B** (blue intermediate washed with acetone) and **C** (**B** washed with water).
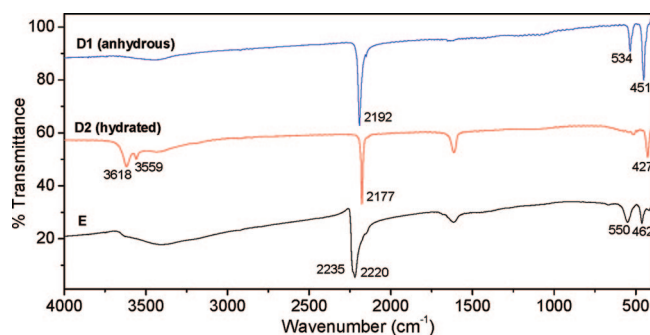

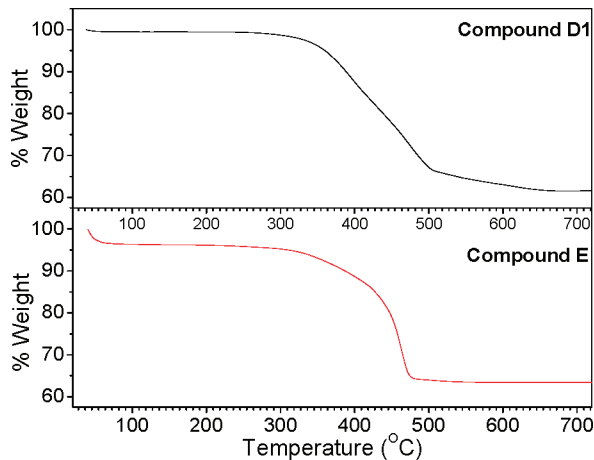**Figure 6.** IR spectra of anhydrous and dehydrated **D** and **E**.

Figure 7. TGA of compounds **D1** and **E** with a 1° min^{-1} ramp rate.
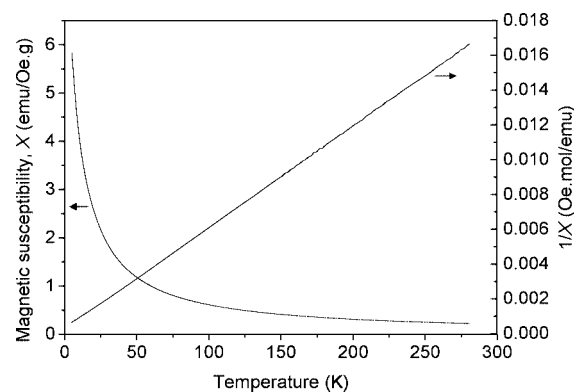

Figure 8. Magnetic susceptibility of compound **D1** (left axis) and its inverse (right axis) as a function of the temperature measured at 10 000 Oe.
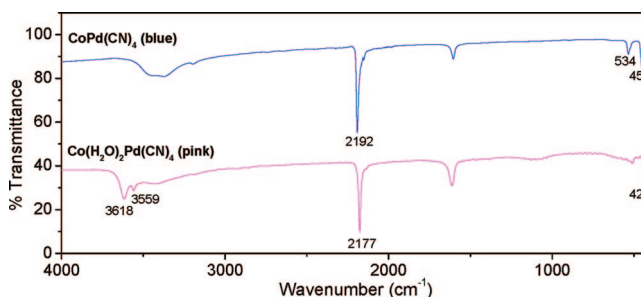

Figure 9. IR spectra of CoPd(CN)$_4$ and Co(H$_2$O)$_2$Pd(CN)$_4$·4H$_2$O prepared from CoCl$_2$ and K$_2$Pd(CN)$_4$. Note that the spectra have the same features as those of **D1** and **D2** in Figure 6.

previous studies of compounds with this structure type.[7,28,37] However, a truly definitive hydrogen model must await a better crystal and/or neutron diffraction.

Co(H$_2$O)$_2$Pd(CN)$_4$·4H$_2$O was found to lose water quite readily. Upon exposure to air, it changed color slightly, suggesting the loss of waters of hydration, but upon mild heating (50 °C) or upon drying at ambient condition on a low humidity day, it changed into the blue form CoPd(CN)$_4$ (Figure 10). A list of *d* spacings and relative intensity obtained from a powder pattern of CoPd(CN)$_4$ is included in Table 2. However, we were

unable to match this pattern to a structural model. Suspending the blue crystals in an atmosphere with 100% relative humidity at 70 °C or placing them in liquid water did not lead to rehydration. However, the blue crystals could be dissolved in excess water upon heating, forming a faint pink solution, from which pink crystals could be recrystallized.

The second loss of CN ligands involves the reduction of intermediates CoPd(CN)$_4$ and Pd(CN)$_2$ to metal. The first appearance of a metallic product in the microwave experiments was observed at 25 s, when small Pd peaks were detected. The metallic product became more obvious at 30 s (Figure 3); the peaks corresponded to the pattern of Pd but had a broader base, suggesting either the presence of very small crystallites or phases with a slightly smaller and slightly larger unit cell than Pd. The

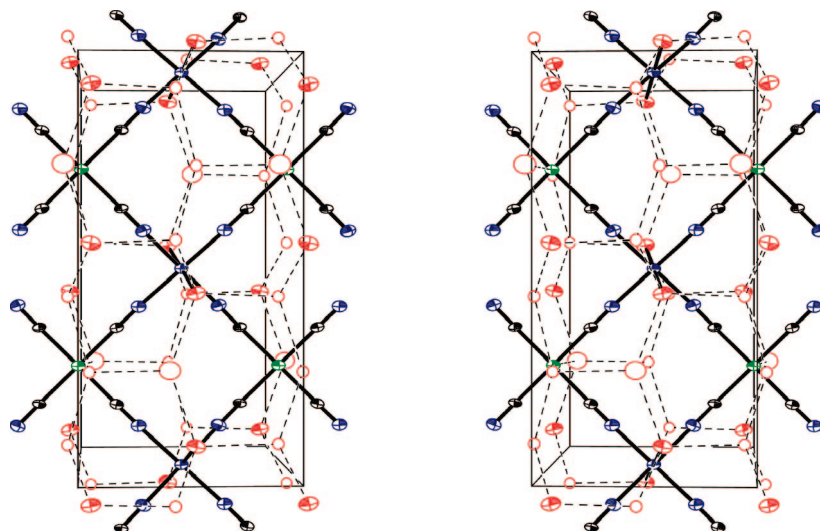(37) Ham, W. K.; Weakley, T. J. R.; Page, C. J. *J. Solid State Chem.* **1993**, *107*, 101–107.

Figure 10. Stereoview of the polymeric structure of CoPd(CN)$_4$ sandwiched between layers of hydrogen-bonded water molecules. All covalently bound atoms are depicted with 50% probability ellipsoids. Water oxygen O(4) is in close contact with Pd(1) and is depicted with an open ellipsoid. The remaining waters are not involved in metal interactions and are drawn as open spheres to aid in their identification. Color scheme: Pd, green; Co, blue; C, black; N, blue; and O, red.

Table 2. d Spacing and Relative Intensity of Peaks in XRD Powder Pattern of CoPd(CN)$_4$

d spacing	relative intensity
6.75413	13.1
6.19430	11.4
4.57389	100.0
4.19464	7.8
3.56335	34.3
3.47699	43.5
3.38409	16.6
3.12506	8.7
3.10053	10.9
2.97635	6.5
2.82836	6.3
2.75729	7.1
2.63636	4.2
2.50253	5.1
2.43020	18.8
2.34697	21.3
2.29489	15.6
2.26264	5.7
2.21710	4.9
2.12497	8.2
2.01204	5.5
1.98951	9.6
1.91126	6.9
1.86291	6.8
1.79058	5.9
1.78852	6.0
1.74305	7.5
1.69763	6.3
1.67925	7.2
1.63426	7.3
1.52749	7.5
1.49574	5.6
1.44545	5.6
1.32733	4.7

attraction of a portion of this product to a magnet indicated the presence of a ferromagnetic phase, which suggested the presence of a Pd–Co alloy. Between 30 and 70 s, it became obvious in IR that, with an increasing irradiation time, the intensity of the peaks above 2200 cm^{-1} corresponding to **E** became lower relative to the 2192 cm^{-1} peak characteristic of **D**.

In XRD, three distinct FCC phases were present in the pattern at 40 s, indicated by three sets of characteristic FCC peaks (111), (200), and (220) (Figure 3B). The peaks in the middle overlaid peaks for pure Pd. The peaks shifted to higher angles from Pd can be assigned to a Pd–Co alloy. The peaks shifted to the left belonged to a phase with a slightly larger unit cell ($a = 3.95$ Å) than Pd ($a = 3.8874$ Å), believed to be PdH$_x$. The origin of hydrogen is unclear. We speculate that hydrogen was either an impurity in the native gel or was formed *in situ* from residual water, but a careful study would be needed to answer this question. By 50 s, the peaks of the Pd–Co alloy and PdH$_x$ had grown at the expense of pure Pd. Between 50 and 70 s, the Pd–Co alloy became the predominant phase. Finally, after 4 min of microwave irradiation, the sample completely converted to a Pd–Co alloy and its IR contained no CN peaks.

Because **D1** and **E** are intermediates in the thermally induced autoreduction of cyanogel to alloy, the thermolysis of both compounds was investigated using comparable masses. The mass loss in **D1** monitored by TGA (Figure 7) started around 300 °C and added to 38%. XRD of the product of heating of **D1** at 650 °C for 2 h showed a FCC Pd–Co alloy with a lattice parameter ($a = 3.753$ Å) corresponding to the composition of 50% Pd.[38] The mass loss in **E** after dehydration started at a slightly lower temperature than in **D1** and was completed earlier (Figure 7). The total mass loss after dehydration was 34%. XRD of the product of heating of **E** at 650 °C for 1 h showed Pd with a small amount of Co (~4%), most likely originating from a trace amount of **D1**.

The formation of a single alloy product upon heating of the Pd–Co cyanogel at 650 °C suggests that the metal products formed upon decomposition of **D** and **E** must interdiffuse to form one alloy product. To test if interdiffusion of Pd and Co at 650 °C occurs, **D1** and **E** were mixed in a mortar and then heated at 650 °C for 1 h. XRD of the product showed FCC peaks corresponding to a Pd–Co alloy containing 10% Co skewed toward higher angles and another set of small peaks

(38) Matsuo, Y *J. Phys. Soc. Jpn.* **1972**, *32*, 972–978.

corresponding to an alloy with 34% Co. The products were clearly different from the products of separate heating of **D1** and **E**.

Discussion

The mass loss observed in the washed gel below 250 °C most likely corresponds to the loss of one CN unit per Co atom in the polymer, causing the reduction of Co^{3+} centers to Co^{2+}, while CN is oxidized to $(CN)_2$. If we maintain the 4:3 ratio of Na:K for a 2:1 Pd/Co cyanogel reaction mixture, then the formula of the dehydrated 2:1 Pd/Co cyanogel polymer is $[Na_{12/7}K_{9/7}(PdCl_2)_2Co(CN)_6]_n$ with a molecular weight of the monomer unit of 659 g/mol. The loss of 1 CN (26.0 g/mol) per unit of dehydrated polymer then corresponds to a mass loss of 3.9%, which is the mass loss observed in our experiment.

The IR and XRD data of various stages of microwave irradiation and the analysis of the intermediates present between the two CN losses in the autoreduction show that very significant changes occur rather suddenly on the Co center during the first CN loss in the reaction. These changes are indicated by changes in the CN and Co–C stretch in the IR spectra and the formation of Co^{2+} detected by UV–vis. Two different cyanide-containing species (**D1** and **E**) occur as intermediates. On the basis of its IR features and its TGA, **E** was identified as $Pd(CN)_2$. Blue **D1** was identified as $CoPd(CN)_4$ possessing a pink hydrated form $Co(H_2O)_2Pd(CN)_4 \cdot 4H_2O$ (**D2**) with a layered structure crystallizing in the *Pnma* space group. The structure of anhydrous $CoPd(CN)_4$ could not be solved because of the inability to obtain good crystals. However, considering its stoichiometry, the bridging nature of the CN ligand and the tetrahedral nature of the Co center, it is speculated that the structure consists of a three-dimensional net of pseudo-tetrahedral Co and pseudo-square planar Pd bridged by CN ligands. The observation that the blue crystals are difficult to hydrate also supports the three-dimensional structure, rather than an open two-dimensional one as in $Co(H_2O)_2Pd(CN)_4 \cdot 4H_2O$, which would be easy to intercalate.

The crystal structure of $Co(H_2O)_2Pd(CN)_4 \cdot 4H_2O$ unambiguously showed that the CN ligands are linked to Pd via the C end and to Co via the N end. In the $K_3Co(CN)_6$ precursor to the original gel, the CN ligand is linked to Co via the C end and it is believed that this connectivity is maintained in the gel polymer. This suggests that the high-temperature treatment of the Pd–Co cyanogel coordination polymer results in a reversal of the binding of the CN ligand. This is not an unlikely event, because CN ligand flipping upon heating has been previously reported in Prussian blue,[14,25] its analogues,[26,39] and other CN-containing transition-metal complexes.[27] In the present work, we have not evaluated whether the cyanide ligand inversion is caused by a flip or an alternative mechanism.

$CoPd(CN)_4$ exhibits a CN peak at 2192 cm^{-1} peak, which moves to 2177 cm^{-1} upon hydration to $Co(H_2O)_2-Pd(CN)_4 \cdot 4H_2O$. The changes in color and IR spectra of $CoPd(CN)_4$ upon hydration are attributed to a change in geometry from tetrahedral to octahedral upon coordination of H_2O. According to Nakamoto,[40] an increase in coordination number results in a decrease in frequency of the CN stretch. This is due to the decrease of the effective positive charge on the metal, resulting in weaker σ donation from the slightly

antibonding σ orbital of the ligand and therefore weaker CN bond. In $CoPd(CN)_4$, the $\nu(CN)$ moves from 2192 to 2177 cm^{-1} upon hydration (and increase in the coordination number), which is consistent with this trend.

We can assume that the magnetic moment in **D1** comes entirely from Co^{2+} because Pd^{2+} is typically square planar and therefore diamagnetic. A species with three unpaired electrons is expected to have $p_{eff} = 3.87$,[35,36] which is in good agreement with the value 3.71. Three unpaired electrons on Co^{2+} suggest a tetrahedral or high-spin octahedral geometry. The conversion between the blue and pink forms of **D** upon heating as well as the stoichiometry information obtained from TGA suggest that the dehydrated form of **D** is not coordinatively saturated and is therefore most likely not octahedral. The results of the magnetization measurements are then consistent with the tetrahedral geometry of Co^{2+}.

Thermolysis of $Pd(CN)_2$ and $CoPd(CN)_4$ showed that the two compounds autoreduce to Pd and PdCo alloy, respectively. The monitoring of the reaction progress showed that, in the conversion of Pd–Co cyanogel to Pd–Co alloy, the first metallic product observed in XRD is pure Pd,[11,18] suggesting that $Pd(CN)_2$ starts converting to a metallic product earlier in time than $CoPd(CN)_4$. Its reduction to metal also seems to be completed before that of $CoPd(CN)_4$, as evidenced by IR of the 70 s stage in the microwave experiments, which shows only one CN peak at 2192 cm^{-1} characteristic of $CoPd(CN)_4$. The observation is supported by TGA, where the mass loss in **E** ($Pd(CN)_2$) starts and is completed at a lower temperature than in **D1** [$CoPd(CN)_4$].

XRD of the 20–25 s samples in Figure 3 as well as that of the intermediate **A** indicated that, during the significant rearrangement on the Co center, some Cl^- ligands fall off the Pd center and become incorporated into KCl and NaCl. Analysis of the filtrates from **A** also indicated that some Cl^- is associated with Co^{2+}, forming $CoCl_2$. It is likely that at this stage of the reaction, while Pd^{2+} loses its Cl^- ligands, it gains CN ligands instead, forming the $Pd(CN)_4$ units.

The clear difference between products of heating of the mixture of **D1** and **E** versus the products of separate heating of **D1** and **E** at the same temperature confirms that diffusion in the Pd–Co system at 650 °C is facile enough for the formation of one FCC phase from the mixture of **D1** and **E**. However, the skew of the main peaks and the presence of small peaks of a second FCC phase show that the diffusion was not completed in the allowed reaction time (1 h). Because heating of a 2:1 Pd/Co gel at 650 °C for 1 h leads to just one FCC phase, the observation above suggests that the complete interdiffusion of Pd and Co is more readily achieved during heating of the mixture **A** produced directly from the gel rather than a physical mixture of compounds **D1** and **E**. This can be explained by a more intimate mixing of **D1** and **E** when mixture **A** produced by heating of the gel is unaltered.

The very intimate mixing of **D** and **E** in the intermediate **A** is supported by further observations. First, EDX line scans of **A** indicated a fairly homogeneous distribution of Pd and Co, which suggests that **D1** and **E** are very finely dispersed in **A**, possibly even part of one polymer chain. Second, separation of **D** from **E** in mixture **B** is rather difficult. During washing of **B**, the first two filtrates were pink and saturated with **D**, suggesting **D** was simply washed out of the mixture. However, four later filtrates were almost clear but still contained a small amount of **D**, which may indicate that some **D** was slowly formed, probably by hydrolysis of **B**. Third, the inability to convert the blue

(39) Brown, D. B.; Shriver, D. F. *Inorg. Chem.* **1969**, *8*, 37–42.
(40) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 5th ed.; Wiley-Interscience: New York, 1997.

crystals of CoPd(CN)$_4$ back to the pink form Co(H$_2$O)$_2$-Pd(CN)$_4$·4H$_2$O upon exposure to liquid water contrasts the conversion of solid **B** to a pink/beige solid **C**. The observation suggests that **D** in mixture **B** either contains extremely small crystals, which can be easily penetrated by water molecules, or is amorphous or completely integrated into the polymer network and its Co^{2+} centers are well-accessible to H$_2$O ligands.

Proposed Mechanism of Autoreduction of 2:1 Pd/Co Gel into Pd−Co Alloy. On the basis of the experimental evidence presented here and previously,[11,18] the following sequence of steps for the decomposition of the 2:1 Pd/Co gel is proposed:

(1) Initial heating of the gel, the formula of which is reasonably assumed to be [K$_{(3-a)}$Na$_a$Co(CN)$_6$(PdCl$_2$)$_2$·xH$_2$O]$_n$, leads to the loss of water based on evolved gas analysis and TGA data collected in this work and previously.[11,18]

$$[K_{(3-a)}Na_aCo(CN)_6(PdCl_2)_2 \cdot xH_2O]_n \rightarrow$$
$$H_2O + [K_{(3-a)}Na_aCo(CN)_6(PdCl_2)_2]_n \quad (1)$$
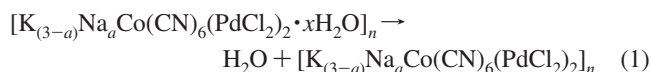
(2) Upon heating to ∼200 °C, exactly one CN ligand per unit of polymer reduces the Co^{3+} center to Co^{2+}, producing half an equivalent of (CN)$_2$. This step is supported by TGA data collected in this work and evolved gas analysis performed previously.[11,18] This first reduction reaction is associated with other significant changes in the polymer:

(a) At least some Cl$^-$ ligands fall off the Pd center, forming NaCl and KCl with the counter-ions of the network and CoCl$_2$ with Co^{2+} formed in the reduction. Detection of NaCl and KCl by XRD after short microwave irradiation and CoCl$_2$ in filtrates from heated gels observed by UV–vis and XRD support this claim.

(b) Some CN ligands originally bound to Co^{3+} become associated with Pd^{2+} (which has lost Cl$^-$ ligands) producing tetracyanopalladate units [Pd(CN)$_4^{2-}$]. Some of these units become covalently associated with Co^{2+}, and some become associated with the residual Pd^{2+}. Evidence supporting this rearrangement is provided by TGA, single-crystal diffraction, and FTIR presented here. The formation of polymeric compounds CoPd(CN)$_4$ and Pd(CN)$_2$ results. The two compounds are intimately mixed, possibly to the extent that they effectively form one coordination polymer containing both Co^{2+} and Pd^{2+} centers.

The chemical equation summarizing the events associated with heating to ∼200 °C is

$$[K_{(3-a)}Na_aCo(CN)_6(PdCl_2)_2]_n \rightarrow$$
$$(CN)_2 + KCl + NaCl + CoCl_2 + Pd(CN)_2 + CoPd(CN)_4 \quad (2)$$
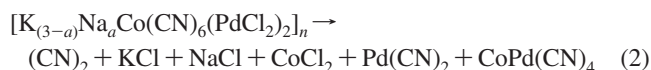
(3) Further heating of the mixture of products leads to further reduction of the cyanide-containing intermediates to metals in zero oxidation states. Particularly, TGA of CoPd(CN)$_4$ and Pd(CN)$_2$, XRD of the products of heating of these two compounds at 650 °C discussed above, and Heibel's analysis of evolved gases[11,18] support this proposed step.

$$Pd(CN)_2(s) \rightarrow (CN)_2(g) + Pd(s) \quad (3)$$

$$CoPd(CN)_4(s) \rightarrow 2(CN)_2(g) + CoPd(s) \quad (4)$$
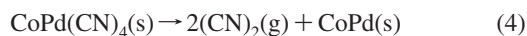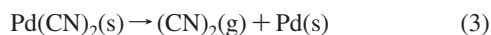
(4) Solid-state diffusion, which occurs concomitantly with step 3, produces one alloy product. This was confirmed by XRD of a thermally reduced physical mixture of CoPd(CN)$_4$ and Pd(CN)$_2$.
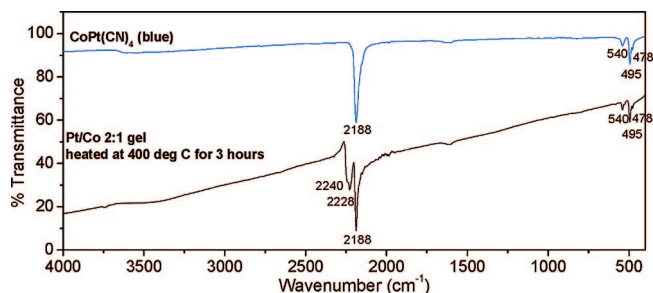
$$Pd + CoPd \rightarrow CoPd_x \quad (5)$$

Figure 11. IR spectrum CoPt(CN)$_4$ made by mixing solutions of K$_2$Pt(CN)$_4$ and CoCl$_2$ (top) and the product of treatment of the 2:1 K$_2$PtCl$_4$/K$_3$Co(CN)$_6$ gel at 400 °C for 3 h (bottom).

Pt−Co Cyanogel-to-Metal Alloy Conversion. Because the cyanogel family consist of many cyanogels with different metal combinations, the study of the 2:1 Pd/Co cyanogel was complemented by the study of the decomposition of the 2:1 K$_2$PtCl$_4$/K$_3$Co(CN)$_6$ gel to show whether the mechanistic scheme presented here may represent a general pathway for the formation of metal alloys from cyanogels. Heating of the Pt−Co gel at 400 °C for 3 h led to the formation of a black product. Its IR (Figure 11) indicated a similar mixture of intermediates as **A** in the Pd−Co system, showing CN peaks at 2240, 2228, and 2188 cm^{-1} and low wavenumber peaks at 478, 495, and 540 cm^{-1}, with a shoulder at 526 cm^{-1}. By analogy to the Pd−Co gel, the 2240 and 2228 cm^{-1} peaks were assigned to polymeric Pt(CN)$_2$, while the 2188 cm^{-1} peak is a signature of CoPt(CN)$_4$. In a control experiment, K$_2$Pt(CN)$_4$ was mixed with CoCl$_2$, forming a pink precipitate, which turned blue upon drying above 100 °C. IR of this compound had peaks at 2188, 540, 495, and 478 cm^{-1}, confirming that this compound was present in the mixture formed by heating the Pt−Co gel at 400 °C. XRD of the mixture indicated the formation of a small amount of Pt metal, suggesting that, at 400 °C, the reduction of the Pt(CN)$_2$ intermediate to Pt had already started occurring. Heating of the gel at 650 °C for 1 h, which is sufficient to completely remove CN ligands from a Pd−Co gel, did not lead to a complete loss of CN ligands, because the signatures of the CoPt(CN)$_4$ intermediate were present in the IR spectrum. Indeed, according to TGA, the decomposition of the Pt−Co gel occurs at slightly higher temperatures compared to the Pd−Co gel. The presented experimental evidence suggests that the decomposition of the 2:1 Pt/Co cyanogel occurs by the same route as in the Pd−Co system.

Conclusions

The progress of the autoreduction of 2:1 Pd/Co cyanogel to alloy was monitored by analyzing different stages of microwave heating of the cyanogel. The conversion involves a sudden change on the Co center, which results in the formation of a blue-colored mixture of cyanide-containing intermediates. These intermediates were prepared by furnace heating at 220 °C, isolated, and identified. The blue mixture produced by heating the cyanogel at 220 °C contains alkali salts, CoCl$_2$, polymeric CoPd(CN)$_4$, and polymeric Pd(CN)$_2$. CoPd(CN)$_4$ possesses a hydrated form Co(H$_2$O)$_2$Pd(CN)$_4$·4H$_2$O, which crystallizes in the orthorhombic crystal system (*Pnma* space group). The structure consists of metal cyanide sheets [square planar Pd(CN)$_4$ units linked to octahedral Co though the N end of the CN ligand] separated by water molecules. The structure of CoPd(CN)$_4$ has not been identified but is speculated to consist of a three-dimensional net of tetrahedral Co and square planar Pd linked

by CN ligands. CoPd(CN)$_4$ and Pd(CN)$_2$ in the blue intermediate are very intimately mixed, possibly even combined in one polymer network, but can be separated because of some solubility of CoPd(CN)$_4$ in water.

On the basis of the available experimental data, a mechanism for the thermal decomposition of the 2:1 Pd/Co cyanogel was formulated. Upon heating to ~200 °C, one CN ligand per unit of the cyanogel polymer is lost as (CN)$_2$, which leads to the reduction of Co^{3+} to Co^{2+}. The CN loss is accompanied by a significant rearrangement, involving the loss of Cl$^-$ ligands from the Pd centers and a reversal of the coordination of the cyanide ligands. This leads to the formation of Pd(CN)$_4^{2-}$ units. Some of these units become associated with Co^{2+}, forming CoPd(CN)$_4$, and some are associated with residual Pd^{2+}, forming polymeric Pd(CN)$_2$. Most likely, CoPd(CN)$_4$ and Pd(CN)$_2$ are in part present individually and combined into one polymer network. Upon further heating, CoPd(CN)$_4$ and Pd(CN)$_2$ decompose independently, but solid-state diffusion causes the formation of one Pd–Co alloy product. CoCl$_2$ and alkali salts are byproducts of the reaction. The 2:1 Pt/Co cyanogel autoreduces by a similar route, suggesting that the mechanistic scheme presented here may represent a general pathway for the formation of metal alloys from cyanogels.

Supporting Information Available: Crystallographic CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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