Synthesis of a Novel Hydrogel Based on a Coordinate Covalent Polymer Network

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Abstract: A new type of polymeric inorganic hydrogel is synthesized from the ligand substitution reaction of K_2PdCl_4 by a cyanometalate such as $K_3Fe(CN)_6$ in aqueous solution. These gels typically contain >95% water, as determined by thermogravimetric analysis. The Pd:Fe ratio is 2:1, independent of the stoichiometry employed, and two chloride ligands are displaced per palladium center. Infrared and electrochemical measurements indicate the presence of bridging cyanide ligands (i.e., Fe–CN–Pd), which lead to the formation of polymeric chains. Interchain cross-links are possible by a number of mechanisms. Dynamic oscillatory rheological measurements were performed during the sol–gel process. The effect of the reactant concentration, Pd:Fe ratio, and concentration of spectator ions on the gelation rate is discussed.

Introduction

Development of an ability to predict and control macroscopic materials properties on the basis of a knowledge of molecular properties is of current interest. Such a capability is of specific interest with respect to condensed-phase materials, due to the technological importance of inorganic solids and polymer systems. One technologically important area of organic polymer chemistry is the construction of hydrogels, integral structures containing sufficiently large quantities of water that the water exhibits bulk properties. While numerous organic hydrogels have been developed, only a limited number of inorganic systems exhibit this property, well-known examples being silica gel and the V_2O_5-based hydro- and aerogels.[1,2] To the best of our knowledge, hydrogelation has not been reported for purely coordinate covalent structures. Datively bonded structures rarely generate the requisite polymeric structure, although there exist limited classes of extended network complexes. Mixed metal cyanometalates (of which Prussian Blue is an example) represent one such class. Although extended network cyanometalates exhibit a high affinity for water, the relatively ordered three-dimensional lattice of these materials, resulting from the octahedral symmetry about the metal centers,[3,4] tends to induce crystallization; thus, a polymeric gel network is not established. Rather, heavily hydrated, microcrystalline phases develop.

We report herein that reaction of a series of mononuclear cyanometalates with square planar $PdCl_4^{2-}$ in aqueous solution produces an extended chain compound which exhibits classic polymer behavior. Upon synthesis, these materials undergo a well-characterized sol–gel transition to produce a hydrogel typically containing in excess of 95% water by weight. Often, synthesis of the initial compound (i.e., prior to the onset of a sol phase) is associated with the production of highly colored materials, which we ascribe to the formation of metal-to-metal (or intervalent) charge-transfer complexes. This type of electronic structure opens the possibility that materials of this type may exhibit useful photochemical properties under appropriate conditions.

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Experimental Section

All Pd complexes and several of the cyanometalates were obtained from either Aldrich or Alfa. $K_4Os(CN)_6$ was prepared from K_4OsCl_6 and KCN as reported by Meyer.[5] $K_4Os(CN)_6$ and $K_4Ru(CN)_6$ were oxidized by reaction with solid PbO_2 and a slight amount of dilute H_2SO_4, followed by filtration, immediately before reaction with $PdCl_4^{2-}$, since the oxidized forms of these species are only stable for about 1 h.[6] $K_4Mo(CN)_8$ was synthesized from MoO_3 as described by Furman.[7] A typical hydrogel was synthesized from the stoichiometric reaction of ~80 mM K_2PdCl_4 with ~40 mM $K_3Fe(CN)_6$ in aqueous solution at room temperature.

UV–vis spectroscopy was performed using an Hewlett-Packard 8450A diode array spectrophotometer, and infrared spectra were recorded between CaF_2 plates in the 4000–400 cm^{-1} range on a Perkin-Elmer 1800 FTIR equipped with a Series 3600 Data Station. A Princeton Applied Research (PAR) 173 potentiostat with a PAR 175 universal programmer and a Houston Instruments XY recorder was employed for the electrochemical studies. These studies utilized a standard three-electrode, electrochemical cell containing platinum working and counter electrodes with an SCE reference half cell. Rheological characterization was performed using a Rheometrics Fluids Spectrometer RFSII in a parallel plate configuration with a gap of 0.750 mm. Time scans were obtained using a frequency of 10 rad/s and a strain setting of 10%.

Results and Discussion

General Observations. When $K_3Fe(CN)_6$ and K_2PdCl_4 are combined in aqueous solution, the resulting mixture immediately turns a dark reddish color. Then, over a period of time, the solution viscosity increases as the sol phase forms. This phase gradually hardens into a polymeric hydrogel, such that a completely linked network has grown between the walls of the container. If appropriate reagent concentrations are employed, the container can be inverted without any disturbance of the gel network. Visually, the product looks like a smooth, solid gelatinous material; however, it cannot be cut cleanly with a knife. When this is attempted, the gel fragments and smears. After the gel has formed, it slowly loses water over a period of a few hours and shrinks in volume. Thermogravimetric results indicate that the hydrogel is composed of 99% water immediately upon formation and then eventually stabilizes at 96%. Attempts to add additional water into the gelatinous structure proved unsuccessful once the gel had formed.

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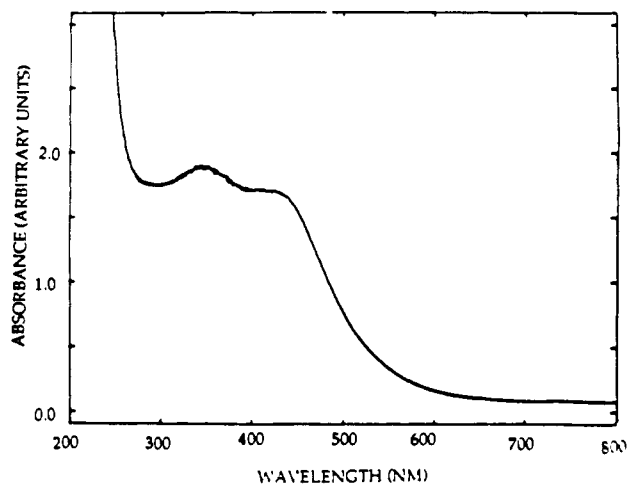(7) Furman, N. H.; Miller, C. O. *Inorg. Synth.* Audrieth, L. F., Ed. **1950**, *3*, 160.

Figure 1. Electronic absorption spectrum of a 2:1 mixture of K_2PdCl_4 and $K_3Fe(CN)_6$ in aqueous solution.

MOLE FRACTION (Pd)

Figure 2. Absorbance (500 nm) versus mole fraction of Pd when K_2PdCl_4 and $K_3Fe(CN)_6$ are mixed in aqueous solution.

Similar hydrogels form when K_2PdCl_4 is reacted with $K_4Fe(CN)_6$, $Na_2Pt(CN)_6$, $K_3Ru(CN)_6$, $K_4Ru(CN)_6$, $K_3Os(CN)_6$, $K_2Co(CN)_5$, and $K_4Mo(CN)_8$. Likewise, gel-like materials result from the reaction of $K_3Fe(CN)_6$ with $PdCl_2$ and K_2PdBr_4 but not with $PdSO_4$, $Pd(OH)_2$, or $K_2Pd(CN)_4$. Platinum species such as K_2PtCl_4 do not produce hydrogels under similar reaction conditions. This reactivity pattern argues for halide loss from the Pd(II) center, allowing for the formation of bridging cyanide linkages. The susceptibility of the chloride ligands of K_2PdCl_4 to substitution by aquo species has been reported to be 3 orders of magnitude faster than that for K_2PtCl_4.[8] It is also known that $PdCl_4^{2-}$ rapidly forms amino-substituted products when reacted with nitrogen-containing ligands.[9,10] The kinetics of this latter transformation are complex, including direct attack by the ligand as well as attack by solvent.

The gelation process appears to be unaffected by the substitution of D_2O for H_2O. Additionally, gels will still form in aqueous solvent mixtures containing up to ^ % (by volume) of an aprotic solvent, such as DMSO, acetoni^ ^, or acetone. A gel which is dehydrated in vacuo does not r ,vell when stirred in deionized water. If such a mixture is vacuum-filtered to remove the Pd/Fe complex and the filtrate is then treated with $AgNO_3$, AgCl precipitates. The amount of AgCl formed (gravimetrically monitored) indicates that ~2 chlorides per Pd are displaced in forming the inorganic hydrogel. This finding supports the hypothesized lability of the Pd center as the primary process associated with polymeric gel formation.

Infrared spectra of the gel and of the dehydrated power yield two strong stretches in the 2000–2200 cm^{-1} window at ~2115 and ~2180 cm^{-1}. These peaks are assigned as terminal and bridging Fe(III)–CN stretches by analogy to similarly bridged species.[11,12] Thus, chloride loss can be associated with the formation of bridging cyanides. In addition, since the cyanide stretching frequencies are sensitive to the iron oxidation state, it can be concluded that the polymer synthesis does not involve a redox reaction. This finding is consistent with the standard redox potentials of $Fe(CN)_6^{3-/4-}$ (0.19 V vs SCE) and $PdCl_6^{2-}/PdCl_4^{2-}$ (1.23 V vs SCE).[13]

Figure 1 provides the electronic absorption spectra for the stoichiometric mixture of $2PdCl_4^{2-}$ and $Fe(CN)_6^{3-}$ just after

mixing (i.e., prior to gelation) at a Pd concentration of 1.25 mM. Two electronic transitions are present in the product at 350 and 422 nm, the latter band tailing into the red. The molar absorptivities of these bands are on the order of 1500 M^{-1} cm^{-1}. While both these features can be linked to the electronic structure of the starting reagents, the red tail of the 422-nm band is specific to the product species. A Job plot[14] (Figure 2) monitoring the absorbance at 500 nm as a function of mole fraction (Pd) yields a maximum at 0.7 ± 0.1, indicating either a 2:1 (theoretical = 0.67) or 3:1 (theoretical = 0.75) Pd:Fe ratio. The 2:1 ratio is the more likely of the two since a 3:1 ratio would imply that every cyanide ligand is bridging in nature, a result which is nullified by the available infrared evidence. The 2:1 ratio is further supported by rheological experiments, as will be discussed later.

Over a period of several weeks after the formation of the Fe/Pd gel, it slowly turns green in color, and then eventually blue, and fragments into smaller gelatinous pieces, expelling water. This decomposition is only observed for gels in which the Group 8 cyanometalate is in the oxidized form. $Fe(CN)_6^{3-}$, $Ru(CN)_6^{3-}$, and $Os(CN)_6^{3-}$ are known to undergo decomposition[6] via cyanide loss to form green or blue mixed-valence complexes similar in composition to Prussian Blue. A similar process is no doubt occurring within the gel network. An infrared spectrum of the green Fe/Pd decomposed gel contains peaks at 2062 and 2117 cm^{-1}, corresponding to bridged Fe(II) and terminal Fe(III)–CN stretches, respectively. Thus, the presence of both oxidized and reduced Fe centers is observed in the decomposition product(s), as expected for a Prussian Blue-like material. Gels containing Group 8 metals in the reduced state do not undergo this decomposition process. Likewise, decomposition is not observed for platinum-, molybdenum-, or cobalt-based gels.

Rheological Characterization. Rheological measurements were made on the Fe/Pd hydrogel using a dynamic oscillatory method. Since these measurements involve only small sinusoidal mechanical deformations,[15] they do not interfere with the gelation process below the gel point; they are therefore particularly useful for monitoring the structural evolution of the gel network with time. Further, they can provide information about the degree of liquidity or solidity of sol–gel phases as a function of time and can be used to estimate the number of polymer cross-links in the system.

Experimentally, a sinusoidal strain of the form shown by eq 1 is applied to the test sample by the lower parallel plate of the

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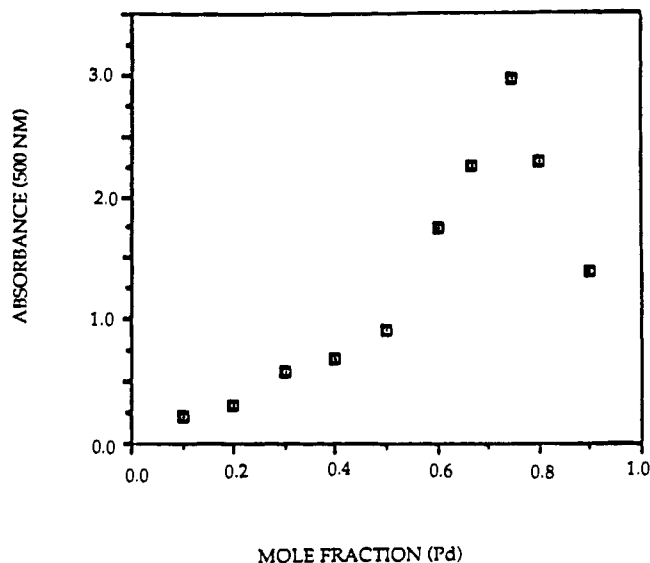
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$$\gamma = \gamma_0 \sin \omega t \tag{1}$$

rheolometer. γ represents the applied strain, γ_0 is the strain amplitude, and ω is the frequency (in rad/s). The plate therefore exerts a small torque on the sample. The upper parallel plate attempts to compensate for this force by rotating in the opposite direction. The amount of force, τ, needed to counterbalance the induced strain is given by eq 2, where G' and G'' represent the

$$\tau = G'\gamma_0 \sin \omega t + G''\gamma_0 \cos \omega t \tag{2}$$

storage (or elastic) and loss (or viscous) moduli, respectively, and correspond to the in-phase and out-of-phase components of the resulting stress.

The kinetics of the gelation process can be measured by monitoring G' as a function of time. For the formation of a gel from an aqueous solution, the storage modulus is expected to initially increase following a sigmoidal function as cross-links begin to form and then level out after the network has been completely constructed. An inflection in the elastic modulus versus time (which is sharper for faster-gelling systems) is therefore observed at the gel point. (The gel point occurs precisely when the last cross-link is made which links the entire network of molecules together so that they become space-filling.) After this point has been reached, part of the network will break down under the application of a sufficiently large strain, leading to a leveling off or slight decrease in the value of G'. A typical response curve for the system of interest is shown in Figure 3 for the reaction of 75 mM $PdCl_4^{2-}$ with 25 mM $Fe(CN)_6^{3-}$.

Using a 3:1 Pd:Fe ratio, the effect of the overall concentration of the reactants on the gel time was investigated. The results are shown in Figure 4, plotted as gel time vs $[PdCl_4^{2-}]$; the resulting curve is best described by a hyperbola. It is not at all surprising that the gel time decreases with increasing concentration since both polymer formation and interchain cross-linking are expected to involve bimolecular processes. However, the shape of the concentration-dependence curve indicates that the kinetics of the cross-linking process are quite complicated.

In a second set of experiments, the overall concentration of the reacting mixture was held constant while the Pd:Fe ratio was varied. A plot of gel time vs Pd:Fe ratio is shown in Figure 5. It is approximately parabolic in nature, with a minimum at a 2:1 Pd:Fe ratio. This observation confirms the Job plot conclusions presented above.

Additionally, it was found that as the ratio of Pd:Fe decreases, G' rapidly decreases after the gel point, whereas at higher Pd:Fe ratios, G' continues to rise slowly even after the gel point has been reached (Figure 6, top). A sudden drop off of the elastic modulus after gelation indicates that the applied strain of the measurements has irreversibly broken the structure, indicating that it is brittle. In less brittle (or self-healing) gels, the system can repair induced fractures almost as quickly as they are formed, leading to a steady increase in G' with time. A plot of G' and G'' vs frequency taken after the gel point has been reached illustrates this point. In a solution, both G' and G'' decrease with decreasing frequency, but the elastic modulus relaxes more rapidly. In a perfect gel, however, the stresses cannot relax and therefore remain constant with frequency, hence G' dominates. Figure 6, bottom, shows the dependence of the moduli on frequency for the two examples mentioned above. When the Pd:Fe ratio is high, the gel is able to respond to the applied strain, and consequently its frequency scan is typical of a stable gel. On the other hand, when more Fe is present than Pd, the gel fractures under the strain, and the resulting frequency scan indicates that the network has been destroyed. It is therefore the cyanometalate which contributes more to the rigidity of the gel network than does the palladium species. This finding suggests that polymer strand cross-linking is affiliated with the cyanometalate centers.
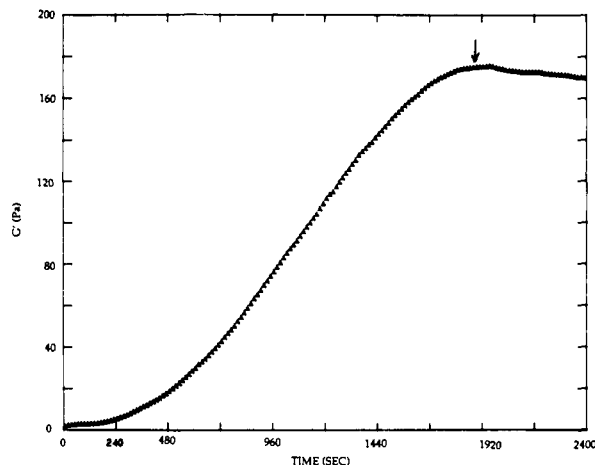

Figure 3. Plot of the elastic modulus (G') versus time for the formation of the Fe/Pd gel at a Pd concentration of 75 mM and a 3:1 Pd:Fe ratio. The arrow indicates the gel point.
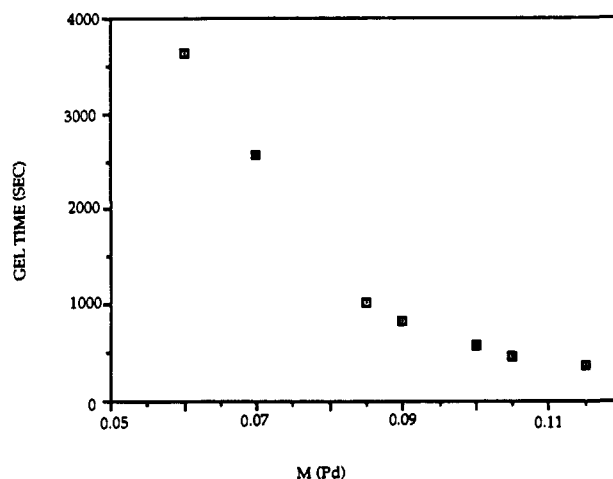

Figure 4. Gel time versus concentration of Pd for the formation of the Fe/Pd gel at a 3:1 Pd:Fe ratio.
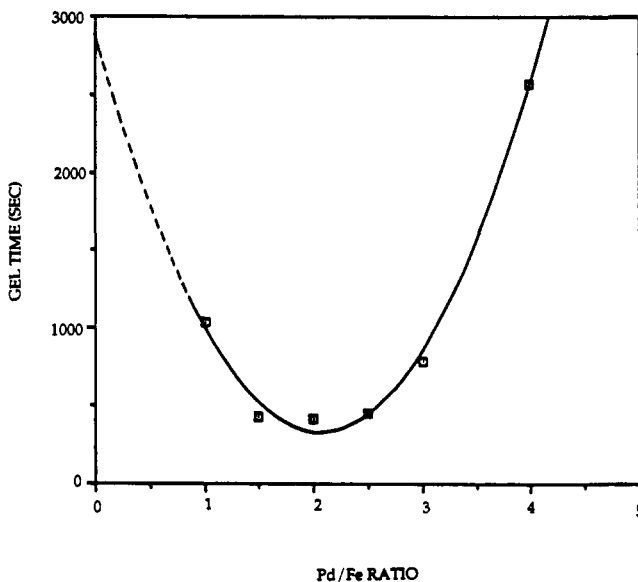

Figure 5. Gel time versus Pd:Fe ratio at an overall concentration of 120 mM.

Dynamic oscillatory measurements can also provide an estimate of the number density (n) of interchain cross-links in a polymer gel network, according to eq 3.[15] G_{en} is due to the contribution of polymer entanglements to the value of G' (and is usually small, i.e., $\sim$1 Pa), k is Boltzmann's constant, T is the absolute
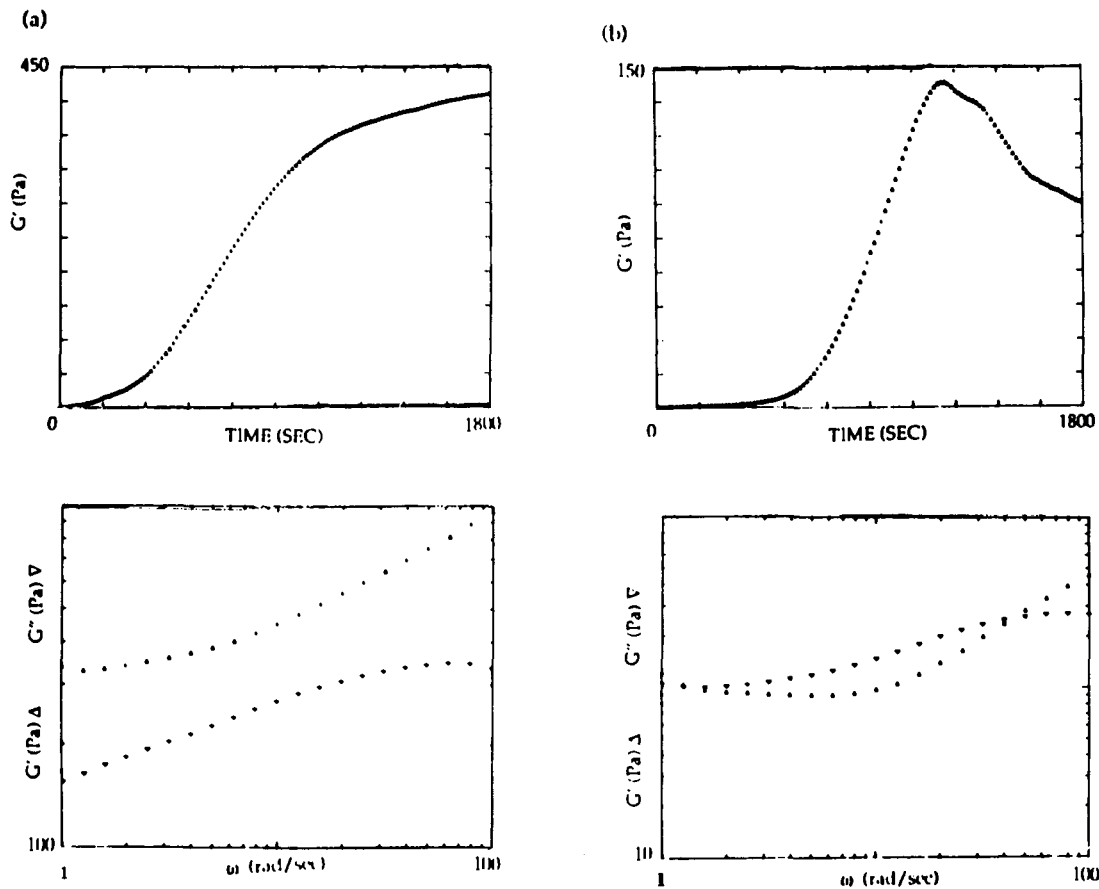
(a)

(b)

Figure 6. G' versus time and $G'.G''$ versus frequency plots for a Pd:Fe ratio of (a) 1.0 and (b) 3.0. The overall concentration was maintained at 120 mM.

$$G' = gnkT + G_{en} \qquad (3)$$

temperature (298 K), and g is a constant between 0.6 and 1. Using eq 3 with $G_{en} = 0$, $g = 1$, an experimentally derived average $G'_{max} = 230$ Pa, and concentrations of 90 mM Pd and 45 mM Fe, a value of 9.2 × 10^{-5} M is obtained for n. In other words, there is one interchain cross-link per 10^3 Pd ions present.

The dynamics of gel formation are also affected by the ionic strength of the solution. For example, when differing amounts of KCl were added to a mixture containing 88 mM Pd and 44 mM Fe, both the gel times and the elastic modulus decreased as the KCl concentration increased (Table I). Thus, while the gel structure formed more rapidly, the final structure was less "solid-like" as the KCl concentration increased. In a qualitative experiment in which a 2:1 Pd:Fe ([Pd] = 70 mM) ratio was employed to synthesize the gel in a saturated NaCl solution, the gel time was decreased by a factor of ~12. This effect is also observed when K_2SO_4, K_3PO_4, $MgCl_2$, or $NaClO_4$ was added to the reaction mixture. In order to determine whether it was the cation or anion which influences the gelation time, a study was performed using 0.5 M concentrations of the ions above and a Pd gel concentration of 70 mM. All of the species gelled within 10 min (as opposed to ~40 min in the absence of added salt). The rate of gelation decreased in the following order: $K_3PO_4 >$ $K_2SO_4 > KCl > NaCl > NaClO_4 > MgCl_2$. Since $MgCl_2$ has less of an effect on the gelation rate than NaCl and $K_3PO_4 >$ $K_2SO_4 > KCl$, one can conclude that the number of cationic species serves to decrease the gel time. However, the relative reactivity trend also suggests that the charge on the anion (not the number of anions) may affect reaction rates. Added chloride apparently does not appreciably suppress polymerization, via perturbation of a hypothetical Pd–Cl $\rightleftharpoons$ Pd^{2+} + Cl$^-$ equilibrium toward the reactant side, thereby blocking the formation of Pd–NC–Fe bridges. Rather, the added cations must be enhancing

Table I. Effect of KCl on the Gel Time and Strength of the Pd/Fe Hydrogel

concn PdCl$_4^{2-}$ (M)	concn Fe(CN)$_6^{3-}$ (M)	concn KCl (M)	G' at 1200 s (Pa)	gel time (s)
0.088	0.044	0.00	2710	925
0.088	0.044	0.25	2640	635
0.088	0.044	0.33	2060	500
0.088	0.044	0.50	1840	415
0.088	0.044	1.50	1500	300

the bimolecular interactions of the two anionic reagents. The cations may facilitate interchain cross-linking by helping to hold the anionic polymer chains in close proximity to each other. However, electrostatic cross-linking of this type apparently does not lead to a robust gel structure, based on the observed decrease in G'.

Electrochemistry. If a cyclic voltammogram is taken immediately upon reaction of 2 equiv of K_2PdCl_4 and 1 equiv of $K_3Fe(CN)_6$ (prior to gel formation) in 0.5 M NaNO$_3$ supporting electrolyte over the potential window from −0.3 to +1.1 V vs SCE, a quasireversible wave is observed at $E_{1/2} = +0.88$ V vs SCE and a nonreversible reduction peak occurs at +0.12 V vs SCE (Figure 7). The peak current of each wave increases with time to a maximum and then begins to decrease gradually (not shown) after the sol–gel transition occurs. At the same time, a nonreversible oxidation wave grows in at +0.70 V vs SCE. The waves centered at +0.88 V vs SCE are assigned to the Fe(II/III) couple of the Pd-bound species. These waves are shifted ~700 mV from that of free [Fe(CN)$_6$]$^{4-/3-}$. Positive shifts of this nature are common for cyanometalate species, since coordination of the bridging cyanide lone pair to a second metal facilitates metal–cyanide back-bonding, thereby making the metal center more
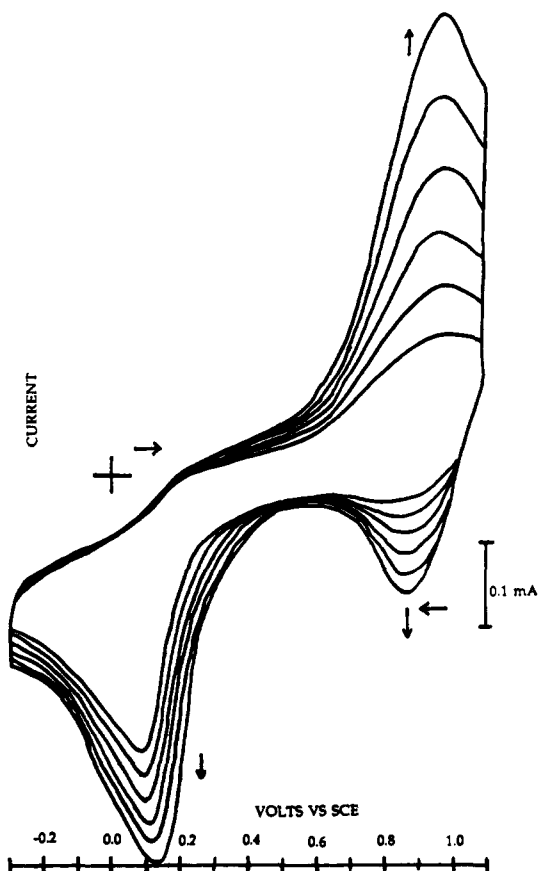
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Figure 7. Cyclic voltammetry of the gelling solution in 1 M NaNO₃ supporting electrolyte using a Pt working electrode at a scan rate of 200 mV/s. The scans are taken continuously, and the direction of growth of the peaks with time is indicated by the vertical arrows. Horizontal arrows indicate the direction of the scan. 0 V vs SCE is marked with a cross.

Chart I

difficult to oxidize.[16] If a Ru/Pd polymer is synthesized, then the quasireversible wave is shifted positive with respect to the Ru(CN)₆⁴⁻/³⁻ redox potential by almost the same amount to +1.33 V vs SCE. No other cyclic voltammetric features are affected by this substitution. The nonreversible reduction peak at +0.12 V vs SCE is ascribed to reduction of the Pd(II) species to Pd metal. This assignment is supported by the observation of a Pd black layer on the electrode surface when the electrode is held at this potential. One possible explanation for the initial increase in peak currents with time is that the surface area of the electrode is effectively increased as Pd(0) is produced. Consistent with this conclusion, if the electrode potential is scanned only between +0.4 and +1.1 V vs SCE, no changes in the heights of the quasireversible waves are observed, since reduction of Pd(II) does not occur in this potential window.

As indicated above, upon gelation a marked change in the cyclic voltammogram is observed, with the waves centered at +0.88 V vs SCE (Fe^{III/III} couple) showing a decreased peak current. As the gel begins to form, the Fe centers appear to lose their ability to interact with the electrode surface. Presumably, this is due to the immobilization of iron sites in the gelatinous network. At the same time, a nonreversible oxidation wave at +0.70 V vs SCE grows in at a Pt electrode whose potential is
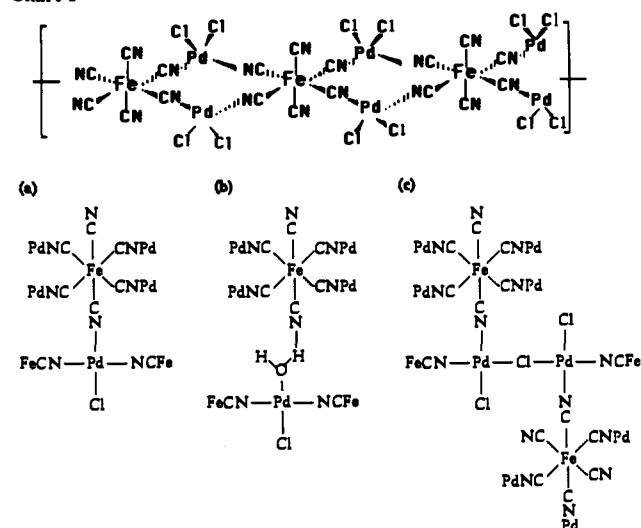
cycled between −0.2 and +1.2 V vs SCE during the gel forming process. This peak is assigned as a Pd(0)-to-Pd(II) oxidation (reported literature value: +0.67 V vs SCE)[13] at the Pd-plated Pt electrode. A similar wave is observed when a Pd working electrode is employed in a KCl supporting electrolyte, cycling its potential over the same window. Presumably, the peak increases with time as a result of the increasing amounts of Pd metal being formed by the nonreversible reduction at +0.12 V vs SCE. If the potential of the gelling solution is scanned between +0.4 and +1.1 V vs SCE, where this reduction is thermodynamically impossible, the redox wave at +0.70 V vs SCE is not observed, corroborating the available evidence for its assignment as Pd(0) to Pd(II).

Conclusions

One possible chainlike structure for the Pd/Fe gel consistent with the data presented is shown in Chart I. Since substitution of two Pd chloride ligands by the N-terminus of the bridging cyanide is expected to follow the trans effect, the cis isomer should result. In keeping with the 2:1 Pd:Fe ratio, four bridging cyanide ligands per Fe center are predicted. Bridging can occur along both the x and y axes to form a long polymeric chain. Kinks in this structure are possible when substitution is trans at the Pd center. Three possible types of interchain cross-links (see Chart I) are conceivable: (1) a third Pd–NC–Fe bridge, (2) a hydrogen-bonded CN–HOH–Pd bridge, or (3) a Pd–Cl–Pd bridge. Since the number density of interchain cross-links is very small (i.e., one cross-link for every 10³ Pd(II) on the average), the nature of the interchain bonding interaction is below the detectable limits for the IR spectroscopic and elemental analysis techniques employed. However, we speculate that an interchain cyanide linkage is the most likely bonding format, with an elaborate hydrogen-bonding network between the remaining terminal cyanides, entrapped water molecules, and chloride ligands providing additional support to the gel structure.

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