

## CYANOGENS: COORDINATION POLYMER HYDROGELS HAVING APPLICATIONS IN MATERIALS CHEMISTRY

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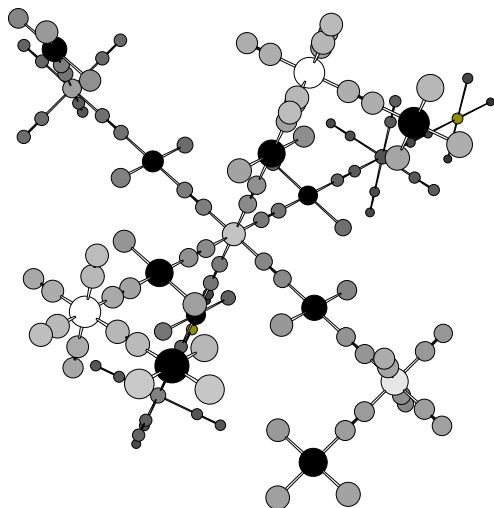
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### Introduction

Within the realm of inorganic chemistry, the formation of hydrogel structures is empirically limited to metal oxides and their related hydroxides. Thus, for example, silica systems containing colloidal particles composed of  $\{\text{Si-O-Si}\}$  polymers lead to the formation of silica gel. Likewise, many first row transition metals based oxides/hydroxides are reported to undergo hydrogelation. Similar chemistry, is not observed for classic inorganic coordination complexes (and their related polymers). These species which tend to be highly charged with good packing geometries either readily dissolve in aqueous solution or produce crystalline solids. However, we have found that the relatively simple ligand substitution reaction which occurs between certain metal chloride compounds and transition metal cyanometalate complexes gives rise to coordination polymers which have a propensity to form hydrogels at room temperature after a short (minutes) reaction period. The reaction involves the substitution of a labile site on the chlorometalate complex by the nitrogen side of a bound cyanide ligand to produce polymeric systems based on the formation of bridging cyanide ligands. The prototypical reaction is the substitution of chloride ligands in the square planar complex  $[\text{PdCl}_4]^{2-}$  as shown in equation (1).



In the case where tetrachloropalladate is reacted with hexacyanocobaltate, we have identified a three dimensional star polymer system <sup>(1,2)</sup> as shown in Figure 1.



**Figure 1.** Cyanometalate polymer formed by the reaction of  $\text{K}_2\text{PdCl}_4$  and  $\text{K}_3\text{Co}(\text{CN})_6$ . Pd centers are shown in black, while Co centers are presented in white. The cyanide ligands (both bridging and terminal are shown in gray as two spheres. The single gray spheres are chloride ligands.

We refer to this class of molecular materials as cyanogels to highlight the bridging cyanide as the structural polymer forming unit and to distinguish them from classical oxometalate inorganic gel systems.

Thermogravimetric analysis indicates that cyanogels are ~95% water by mass. Gels can be dehydrated to form xerogels. <sup>(1,3,4)</sup> Aerogels can be formed by exchange of the aqueous phase by super critical carbon dioxide followed by gasification of the  $\text{CO}_2$ . <sup>(1)</sup>

Thermal processing of either the Pd/Co xerogels or aerogels gives rise to a variety of utilitarian solid-state materials. For example, thermolysis under an inert nitrogen or argon atmosphere produces composition

controlled Pd/Co metallic alloys. <sup>(2,5)</sup>

Such processing can be carried out at temperatures as low as  $500^\circ\text{C}$ . In contrast, standard powder metallurgical synthesis of these material is carried out at temperatures above  $\sim 1800^\circ\text{C}$ . Thermal processing in the presence of oxygen produces the layered ceramic oxide,  $\text{PdCoO}_2$ . Again low temperatures are employed compared to typical solid-state synthesis conditions. <sup>(2,5)</sup>

The bulk properties of the Pd/Co cyanogel system along with an expansion of this chemistry beyond the Pd/Co system is the subject of this report.

### Results and Discussion

**Cyanogel Synthesis.** Here we consider cyanogel systems in which the cyanometalate component is expanded to include the following metals: Cr, Mn, Fe, Ni, Ru, Mo, Pd, Os, W, or Pt. We now report that cyanogels are not only formed when hexacyanometalate reagents are employed, but also form rapidly at room temperature when square planar or eight coordinate cyanometalate complexes are utilized. It is also found that a second class of cyanogels, referred to as type II cyanogels can be formed by employing the dicyanamide ligand in place of the cyanide ligand. In addition, we have evaluated the chemical synthesis of type I (i.e. cyanide containing) cyanogels via the reaction of hexacyanometalates (metal = Co or Ru) with metal chloride species other than tetrachloropalladate. Tetrachloropalladate appears unique with regard to reactivity at room temperature. However, if aqueous solutions of either  $\text{RuCl}_3$  or  $\text{IrCl}_3$  are reacted at temperatures in the  $50\text{-}60^\circ\text{C}$  range polymer formation followed by sol formation and gelation are observed. We correlate the temperature requirement with the ease of substitution of the chloride ligand. Although not a general reaction, we also find that aqueous  $\text{SnCl}_4$  reacts with ferrocyanide to form a gel at room temperature. This gel is much stiffer than the other cyanogels however, we find that the stoichiometry of this gel and all other gels using a hexacyanometalate reagent is two metal chlorides to one cyanometalate. The thermal processing properties of this gel are similar to the purely transition metal based gels. <sup>(6)</sup>

**Bulk Structural Properties of the Cyanogels.** An understanding of the pore structure of both the hydrogel materials and dehydrated products derived from it are central to the characterization of these materials. To that end, we have undertaken three types of evaluations of the Pd/Co system: SEM analysis of aerogel materials, gas adsorption isotherms of aerogel and xerogel materials, and beam bending experiments of the hydrogel material. The first two techniques are classical characterization methodologies for random, porous materials. The final technique is a novel characterization process developed by George Scherer. <sup>(1)</sup>

The beam bending experiment involves the formation of a stable rod of hydrogel approximately 5mm in diameter and 5-10cm in length. The hydrated rod is placed in a water bath and supported at its ends. A screw driven rod is then employed to apply a calibrated load to the middle of the rod and the stress/strain relationship for the rod is observed. Application of the load causes contraction of the upper surface of the rod and expansion of the opposing surface. This initialing induces a flow of water within the gel structure. Thus, the load is initially applied to the aqueous phase of the hydrogel system. Once the fluid dynamics stabilize this load is transferred to the polymer phase of the system. The stress/strain relationship for this system allows one to calculate the permeability of the hydrogel system. This data coupled with the polymer concentration and density data allows a deduction of the average pore size for these systems. We find that the data obtained using this technique are consistent with SEM data obtained on the aerogel system. <sup>(1)</sup> Key findings are that the pore structure is dependent on the concentration of reagents employed, and that pore size varies from  $\sim 50\mu$  to  $\sim 10\mu$  over a reactant concentration range of 0.05M to 1M. The density of the polymer with the hydrogel also varies. However, this variation is solely due to the contraction in pore size with increased reagent concentration. The size of polymer particles is  $\sim 50\mu$ , independent of reagent concentration.

The data reported above, although self consistent, are not consistent with BET isotherm data using both  $\text{N}_2$  and  $\text{CO}_2$  probes. Both gases indicate an average pore size of  $\sim 5\text{nm}$  for both the aerogel and xerogel systems. Surface areas range from  $500\text{-}700\text{m}^2/\text{g}$ ; these areas are gas

independent. No evidence for pore distortion by gas adsorption is observed. However, capillary condensation of carbon dioxide is indicated. The variation in length scales observed between the isotherm data and the beam bending data can be rationalized by postulating the existence of two pore domains. The larger pore size is associated with the inter-particle spacing while the nanoscopic domain is related to the porosity of the molecular polymeric structure. We are currently undertaking a TEM analysis of this system in an effort to verify this conclusion.

**Selective Adsorption of Carbon Dioxide.** One interesting outcome from the gas adsorption data is the possibility that the dehydrated gel systems may act as a carbon dioxide reservoir or filter. That is, these materials may selectively and reversibly adsorb carbon dioxide in the presence of other gases. This hypothesis has been verified by microbalance, pressure swing experiments in which the selective uptake of CO<sub>2</sub> in the presence of Ar, N<sub>2</sub>, O<sub>2</sub> or CH<sub>4</sub> is observed. Co/Pd xerogels can absorb up to 4% carbon dioxide by mass. Similar selectivity is observed for N<sub>2</sub>O and SF<sub>6</sub> suggesting that the observed selectivity is related to the diffusivity of the gas and thus its ability to undergo capillary condensation within the nanopores of the dehydrated cyanogel.

### Conclusions

Cyanogel synthesis is now expanded to include most of the transition metal cyanometalates and to allow for the generation of non-palladium containing polymers. As discussed elsewhere <sup>(7)</sup> this synthetic utility can now be employed to provide a wide variety solid-state products. From a pragmatic point of view the ability to make solid-state materials without palladium content dramatically expands the utility of these systems in the arena of sol-gel processing. Recently, we have taken advantage of this synthetic diversity to provide a sol-gel strategy for the formation of perovskite materials, metal nitrides, and metal sulfides. <sup>(8)</sup> In addition to the versatility of these materials as solid-state precursors, the bulk xerogels and aerogels of Pd/Co cyanogel system have been demonstrated to have a pore network which exists on two length scales, both mesoscopic and nanoscopic. The smaller pore network has been demonstrated to act as a carbon dioxide selective reservoir. This property may have applications in the removal of CO<sub>2</sub> from sealed recirculating atmospheres. The reversible nature of this adsorption process also makes it of interest with regard to carbon dioxide reactivity since it provides a mechanism for delivery high concentrations of this gas to a reactive interface. One possible application under current exploration is the use of this material in an electrochemical system for the reduction of carbon dioxide to methanol.

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