

/ Princeton University Doctoral Dissertations, 2011-2017 (/jspui/handle/88435/dsp01td96k251d)  
/ Chemistry (/jspui/handle/88435/dsp01sf2685121)


Title:	Characterization of the fluid and solid components of cyanogel systems during the gelation process
Authors:	Fortmeyer, Ivy Camille ( <a href="#">/jspui/browse?type=author&amp;value=Fortmeyer%2C+Ivy++Camille</a> )
Advisors:	Bocarsly, Andrew B ( <a href="#">/jspui/browse?type=advisor&amp;value=Bocarsly%2C+Andrew++B</a> )
Contributors:	Chemistry Department
Keywords:	coordination polymer ( <a href="#">/jspui/browse?type=subject&amp;value=coordination+polymer</a> ) cyanogel ( <a href="#">/jspui/browse?type=subject&amp;value=cyanogel</a> ) gelation ( <a href="#">/jspui/browse?type=subject&amp;value=gelation</a> ) NMR spectroscopy ( <a href="#">/jspui/browse?type=subject&amp;value=NMR+spectroscopy</a> ) spectroscopy ( <a href="#">/jspui/browse?type=subject&amp;value=spectroscopy</a> )
Subjects:	Chemistry ( <a href="#">/jspui/browse?type=subject&amp;value=Chemistry</a> ) Materials Science ( <a href="#">/jspui/browse?type=subject&amp;value=Materials+Science</a> )
Issue Date:	2016
Publisher:	Princeton, NJ : Princeton University
Abstract:	The work in this thesis concerns the sol-gel transformation in cyanogel systems comprised of d8 square planar chlorometalates (M=Pd(II), Pt(II)) and d6 octahedral hexacyanometalates (M=Fe(II), Co(III), Ru(II)). The body of this thesis is split into two chapters. The first chapter examines the physical changes in the solvent phase of the sol-gel network, and the second focuses on the polymer backbone of the gel. Studies on the water component of cyanogel systems during the gelation process were carried out with a variety of in situ spectroscopic techniques. The use of high resolution-magic angle spinning nuclear magnetic resonance (HR-MAS NMR) to identify and characterize different water environments was explored, but was ultimately found to disrupt gelation. Standard solution-phase <sup>1</sup> H NMR proved sufficient for calculation and qualitative modeling of spin-spin and spin-lattice relaxations, providing distinct spectral markers of the gelation point and subsequent aging process. Vibrational spectroscopy was used to explore the hydrogen bonding environment of the water during gelation. The kinetics of polymerization of the cyanogel backbone was explored using both in situ and ex situ techniques. Data collected by <sup>13</sup> C NMR and <sup>195</sup> Pt NMR primarily demonstrated first order kinetics, implying a dissociative substitution mechanism at the chlorometalate center. Rate constants for gelation in the presence of various added monopotassium and nitrate salts were calculated. Added chloride was found to significantly slow gelation and was further explored using NMR and vibrational spectroscopy. A mechanism was proposed for the polymerization taking into account the dissociative substitution and the bridging geometries implied by <sup>13</sup> C NMR.
URI:	<a href="http://arks.princeton.edu/ark:/88435/dsp01np193c65d">http://arks.princeton.edu/ark:/88435/dsp01np193c65d</a> ( <a href="http://arks.princeton.edu/ark:/88435/dsp01np193c65d">http://arks.princeton.edu/ark:/88435/dsp01np193c65d</a> )
Alternate format:	The Mudd Manuscript Library retains one bound copy of each dissertation. Search for these copies in the library's main catalog: <a href="http://catalog.princeton.edu">catalog.princeton.edu</a> ( <a href="http://catalog.princeton.edu">http://catalog.princeton.edu</a> )
Type of Material:	Academic dissertations (Ph.D.)
Language:	en
Appears in Collections:	Chemistry ( <a href="#">/jspui/handle/88435/dsp01sf2685121</a> )


## View/Download (/jspui/bitstream/88435/dsp01np193c65d/1/Fortmeyer\_

8/15/17, 12:12 PM

Items in Dataspace are protected by copyright, with all rights reserved, unless otherwise indicated.

Search





**Advanced Search** (/jspui/simple-search?location=88435/dsp01sf2685121)

Browse

Issue Date
Author
Academic Advisor
Subject