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Linear Conjugated Coordination Polymers Containing Eight-Coordinate Metal Centers

Ronald D. Archer[a]; William H. Batschelet[a]; Marvin L. Illingsworth[a]
[a] Dept. of Chemistry, University of Massachusetts, Amherst, MA

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Linear Conjugated Coordination Polymers Containing Eight-Coordinate Metal Centers

Ronald D. Archer, William H. Batschelet, and Marvin L. Illingsworth
Dept. of Chemistry, University of Massachusetts, Amherst, MA 01003

ABSTRACT

Two linear coordination polymers are reported in which conjugated organic ligands and nonrigid eight-coordinate metal centers are linked to form macromolecules with molecular weights of greater than 10^4 Daltons. The tungsten(IV) chelate is an inert low-spin d^2 species with four oxygen and four nitrogen donors per metal with two bidentate blocking ligands and one bis-bidentate bridging ligand. The zirconium(IV) chelate is rendered inert through the use of a bis-quadridentate Schiff-base ligand. Future possibilities and potential uses are also discussed.

INTRODUCTION

Over the past quarter century a large number of four- and six-coordinate Werner coordination systems have been investigated for metal-coordination polymers (1-7). Fibers containing coordinated zinc (Enkatherm) (8-9) and greases containing metal phosphinate polymers (10) are examples of thermally stable coordination compounds. However, the vast majority of the systems which have been investigated have suffered from a retention of the brittleness associated with thermally-stable multielement inorganic condensed networks, only moderate oligomerization (due to stacking in planar systems in particular), intractability, or the lack of desired high temperature stability as a result of either organic linkages or weak coordinate bonds. Because the four- and six-coordinate systems typically have rigid coordination spheres, organic single bonds are necessary for flexibility. Unfortunately, the organic bonds which allow rotation are typically less thermally stable than conjugated systems. The latter give thermal stability at the expense of flexibility.

Our approach is to use substitution-inert nonrigid metal centers with thermally stable conjugated bridging ligands. Nonrigid coordination is the rule for coordination number 8 (11-12) because the D_{2d} dodecahedron and the D_{4d} square antiprism polytopes (Figure 1) normally possess very similar energies. Thermally stable and substitution-inert eight-coordinate tungsten(IV) 8-quinolinol chelates (13-16) and zirconium(IV) quadridentate Schiff-base chelates (17) had been synthesized in our laboratory and seemed to be logical bases for thermally stable coordination polymers. [Whereas most d^0 complexes are labile, quadridentate ligands make zirconium(IV) an inert metal center. Low-spin d^2 tungsten(IV) chelates are substitution-inert, even with bidentate ligands.] Ligands initially considered for conjugated bridges were the anions of quinoxaline-5,8-diol and N, N', N'', N'''-tetrakis-(salicylidene)-1, 2, 4, 5-tetraaminobenzene for tungsten(IV) and zirconium(IV), respectively. [Ligands such as phenazine-1,5-diol were ruled out on steric grounds.] Whereas a double headed "bis-quadridentate" Schiff-base ligand completes the coordination sphere for the zirconium species, the "bis-bidentate" bridges would result in excessively

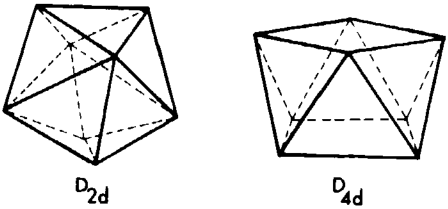


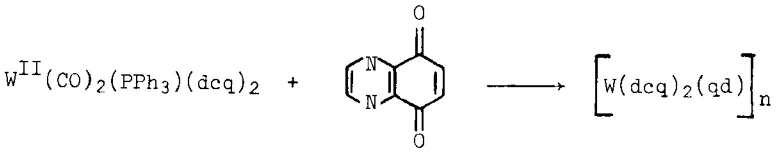
Figure 1. The D_{2d} dodecahedral and D_{4d} square antiprismatic polytopes which are typically of similar energy for eight-coordination complexes.

cross-linked brittle species unless two bidentate ligands are present to prevent the cross-linking. [The small amount of cross-linking desired in polymers will occur by a slight bit of ligand scrambling, which normally occurs in our inert monomer syntheses (18).] Therefore, we have developed specific methods for synthesizing $W(CO)_2$-$[P(C_6H_5)_3](\overset{\frown}{N\,O})_2$, where $\overset{\frown}{N\,O}$ is the anion of an 8-quinolinol derivative (19-20).[These tungsten(II) chelates can be oxidized with a bridging dione to form tungsten(IV)/bridging-diol species. (See below). Alternatively, $W(\overset{\frown}{N\,O})_2Cl_2$ chelates, which we have recently prepared (21), might be allowed to react directly with bridging ligands.

CURRENT STATUS

Tungsten(IV) Polymer

Bis(5,7-dichloro-8-quinolinolato)-5,8-quinoxalinediolatotungsten(IV), which we abbreviate as $[W(dcq)_2(qd)]_n$, has been synthesized by a unique two-electron redox reaction between the seven-coordinate (22) dicarbonylbis(5,7-dichloro-8-quinolinolato)(triphenylphosphine)-tungsten(II) (19) and quinoxaline-5,8-dione (23) in dichloromethane as follows:



Reaction at 0° for 40 hours followed by centrifugation and extraction with more dichloromethane yielded a dark blue polymeric material [which is analogous to the dark colored monomeric tungsten(IV) chelates] with elemental mole ratios within 3% of those anticipated for the infinite polymer (24). Solvation, hydrolysis, and inhomogeniety have precluded more perfect mole ratios. The anticipated coordina-

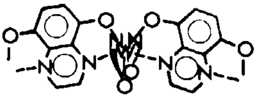


Figure 2. Schematic representation of the $[W(dcq)_2(qd)]_n$ polymer with the 5,7-dichloro-8-quinolinol ligands represented as $\overset{\frown}{N\ O}$. The structure shown is for a mer isomer linkage, but the bifac isomer is also possible (cf., reference 25).

tion sphere about the tungsten atom is shown schematically in Figure 2, with selection of positions (25) based on Orgel's rule (26) for $W(\overset{\frown}{N\ O})_4$ type eight coordinate species.

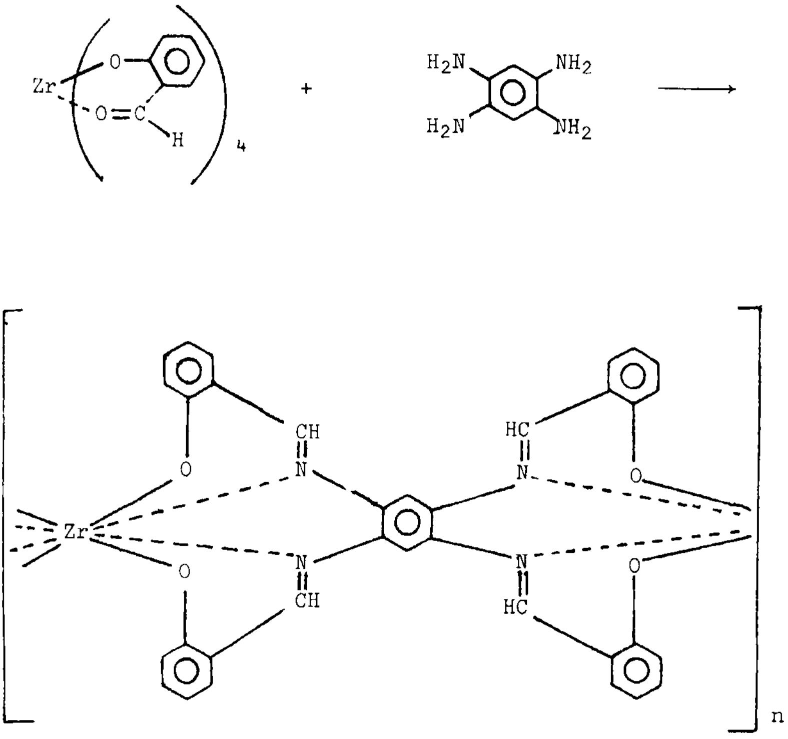
Initial syntheses of the tungsten(IV) polymer at about 40°C led to oligomers with inherent viscosities at about 0.1 dℓ/g. Synthesis at 0° has led to a $[W(dcq)_2(dq)]_n$ polymer with an inherent viscosity of 0.25 dℓ/g for the dimethyl sulfoxide (DMSO) soluble fraction. The viscosity is similar to those observed for organometallic polymers above 50,000 Daltons (27). The analytical results can be fit to such a molecular weight analysis if the terminal groups are hydroxide groups. Metal:ligand ratios are also consistent with such molecular weights. A slow hydrolytic decomposition of this polymer occurs because of the poor nucleophilicity of the qd^{2-} ligand and makes for some variation in analyses.

The polymer appears black in the solid state and blue-black in concentrated solutions. Absorption spectra are given elsewhere (24). Whereas analogous monomeric tungsten(IV) eight-coordinate chelates have strong metal to ligand charge-transfer absorptions near 700 nm (16), the polymer exhibits absorption maxima well down into the near infrared region with a tail on the absorption as low as 3500 cm^{-1}. The possibility of a one-dimensional electron-transfer system with this type of species is intriguing. Furthermore, the analogous tungsten(V) monomers have low energy ligand to metal charge-transfer transitions (28); thus, electron conduction is a distinct possibility, especially for partially oxidized polymers (5).

Thermal analysis of the tungsten polymer in nitrogen indicates an inherently stable polymer with a slow decomposition. Although the decomposition begins near 250°C, the thermal profiles show incomplete decomposition to the oxide, even at 800°C. However, in air decomposition to WO_3 occurs near 510°C, with a partial weight loss even earlier near 230°C. Unfortunately, the nucleophility of the bridging ligand is limited by the presence of two heterocyclic nitrogen atoms in the same aromatic ring. Other bridging ligands which do not possess this weakness are currently under investigation.

Zirconium(IV) Polymer

Because of the low solubility of the Schiff base of 1,2,4,5-tetraaminobenzene and salicylaldehyde, an indirect synthesis was used in which the Schiff-base condensation reaction was made between freshly prepared tetrakis(salicylaldehydato)zirconium(IV) (17) and recrystallized 1,2,4,5-tetraaminobenzene in dry DMSO under nitrogen:



This condensation proceeds reasonably rapidly at room temperature in DMSO. The solvent interacts with the water produced in the reaction sufficiently for considerable polymerization to occur prior to hydrolysis at the zirconium centers. A red glossy material results upon removal of the DMSO.

The elemental analyses show that appreciable DMSO solvent is rigorously held after extensive drying and that excess oxygen is present relative to the infinite chain values, apparently from the water produced in the Schiff base reaction. This excess oxygen is assumed to be hydroxide end groups, which is consistent with the observed OH stretch (3500 cm^{-1}). The number of repeating units based on this assumption is approximately thirty, which corresponds to an average molecular weight near 2×10^4 Daltons. If some of the OH stretch and excess oxygen is due to water, then the molecular weight is higher. In fact, the zirconium to ligand ratio is consistent with approximately fifty-five repeating units per average polymeric molecule, or a molecular weight average closer to 4×10^4 Daltons (24).

An inherent viscosity of 0.15 (dℓ/g) for a 0.1% w/v DMSO solution of the red glassy material is consistent with the view that most of the OH groups are indeed present as end groups; i.e., with molecular weights of 20,000 to 40,000, although K and α haven't been determined for this system to date.

In addition to the OH stretch, the infrared spectrum exhibits a phenyl ring/oxygen stretch at 1310 cm^{-1}, which is shifted from 1280 cm^{-1} in the free bridging ligand. This shift is analogous to the shift observed in the model zirconium Schiff-base chelate, $Zr(dsp)_2$ (17), where H_2dsp = disalicylidene-o-phenylenediamine. Other infrared absorptions are also consistent with the solvated polymer.

Thin films and glassy layers of the zirconium polymer have been prepared. The films diffract light, but show no x-ray diffraction pattern, which is consistent with the amorphous nature of the polymer. At the short chain lengths obtained so far, the polymer appears somewhat brittle. A yellow-orange precipitate is obtained from the addition of acetone to DMSO solutions of the polymer.

Whereas H_4tsb and its derivatives have very limited solubility, the DMSO reaction between Zr(sal)$_4$ and TAB produces an oligomer which is orders of magnitude more soluble. Solvent removal in vacuo or the addition of a miscible nonsolvent such as acetone is necessary to isolate a solid product. Thus the stacking interactions of the aromatic systems have been overcome by the coordination to zirconium. This solubility difference appears to be related to the puckered, perpendicularly arranged, quadridentate ligands anticipated from the model compound x-ray structure (29), in which the ligands show no tendency to stack with either benzene solvate molecules or chelate ligands from adjacent molecules. Models of the polymer chains, assuming the described stereochemistry, also indicate significantly reduced lattice forces. Nonrigid molecular motion may further hinder packing of the polymer chains.

A condensation polymerization using the water scavenger, 2,2'-dimethoxypropane(DMP) was attempted, but no perceivable increase in the average polymer chain length was obtained. Thus, we conclude that DMP did not diminish the rate of chain termination, that imprecise stoichiometry limited the chain growth, or that DMP reacted with one of the other reactants. Further experimentation is necessary.

PROSPECTIVES

The isolation of polymeric species with molecular weights indicative of degrees of polymerization of from 20 to 50 units for step-growth polymerizations which involve either a two electron redox reaction or else a condensation reaction in the presence of a metal ion which can react with water means that the extent of reaction and stoichiometry are $\geq 95\%$. Reactions which are standard reactions for polymer formation could improve the degree of polymerization even further inasmuch as solubility of the polymers in DMSO is still reasonable at room temperature in both cases. Toward that end we have synthesized bis(N,N'-disalicylidene-3,4-phenylenediamine-1-ethylbenzoato)-zirconium(IV)(30). Preliminary reactions designed to form ladder polymers via condensation of aromatic amines to the free ester groups were unsuccessful. The reaction temperatures required (280-360°) to produce aromatic amides and benzimidazoles resulted *in side reactions and lower degrees of polymerization.* The use of catalysts (31-32) should allow much lower temperatures. Conversely, more reactive functional groups could be used. Alternate polymerization modes for the tungsten chelate polymer include the condensation of $W(q)_2(cq)_2$ [where q^- = the anion of 8-quinolinol and cq^- = the anion of 5-chloro-8-quinolinol] with Na_2S analogous to the synthesis of polyphenylsulfide from dichlorobenzene and sodium sulfide. Dilithio derivatives coupled with diiodo derivatives might also be possible, analogous to the polyferrocene preparations noted elsewhere in this volume.

Whereas these studies were initiated toward the end of producing thermally stable polymers, the potential usefulness of these species may be more toward the production of conducting polymers or a related photochemical electron-transfer use. Eight-coordinate tungsten(IV) chelates can be oxidized to analogous tungsten(V) species as noted above and partially oxidized polymers should function as electron carriers. The standard potential for the monomer chelates ranges from +0.2 to +0.4 volts vs. SCE depending on the ligands (33). The fluorescence of the zirconium Schiff-base polymer (34) is indicative of photochemical potential for these species as well. We have synthesized a tungsten(IV) Schiff-base polymer (16), but only in very low yields; therefore, tungsten(IV) Schiff-base polymers have not been investigated to date as no good high-yield pathway has been found. This challenging synthesis could couple the advantages of both systems we have been investigating. Further, the thermal weak points of the zirconium Schiff-base polymer appears to be a reverse reaction around 250°C, which could be avoided by reduction of the Schiff-base double bond with $NaBH_4$.

Overall, we feel that the potential for such chelate polymers has just barely been tapped. Bridging ligands such as 1,5-naphthyridine-4,8-diol and 1,5-diazaanthracene-9,10-diol offer marked nucleophilic advantages over the quinoxalinediol used herein. Synthetic complications have not yet allowed the synthesis of eight-coordinate polymers with these ligands, but the potential is there. New specific syntheses of mixed-ligand molybdenum chelates (35-36) should allow extension of our polymers to molybdenum. The advantage of molybdenum relative to tungsten is a reaction rate increase for molybdenum. Conversely, this implies less thermal stability in a hydrolytic sense. Extension to niobium and/or rheniun for which inert eight-coordinate cyano complexes are known should be obvious. The potential appears almost endless.

ACKNOWLEDGEMENTS

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