

## Problems in the Nomenclature of Inorganic Polymers\*

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Although current proposals for naming polymers as biradicals can be applied in principle to certain inorganic polymers, many coordination polymers cannot logically be considered to have biradical repeat units. The 1957 IUPAC rules for inorganic nomenclature offer a basis for naming coordination polymers; however, the nomenclature of inorganic biradicals has not yet been definitively developed.

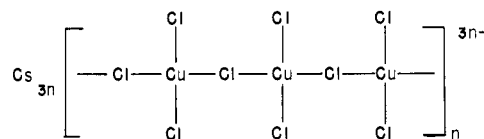
Good progress has been made toward a system for naming polymers with known structures,<sup>2</sup> but it has been designed primarily with organic polymers in mind. A logical starting point in the naming of inorganic polymers is to determine how suitable that system is for application to inorganic polymers.

Strictly speaking, to be termed inorganic, a polymer should contain no carbon. In practice, however, the field of inorganic polymers has come to include many species containing carbon, and the generally accepted criterion for inorganic polymers is that there be no carbon in their backbones. Acceptance of this definition leads to the classification of polymers as organic, inorganic, or semiorganic, depending on whether they contain in their backbones only carbon, no carbon, or at least two elements including carbon, respectively.

The aforementioned rules apply to linear organic polymers and to many semiorganic polymers, but not to all, because there are a number of differences between carbon and other elements. First, a variety of coordination numbers other than four are observed for elements other than carbon. Second, elements other than carbon frequently have variable coordination numbers. Third, some elements, in particular transition elements, have more than one oxidation state. Fourth, there are coordinate covalent bonds of various types, as well as covalent bonds between some elements. Fifth, there are more extensive possibilities for isomerism among some compounds with inorganic centers than for organic compounds. These differences will obviously give rise to problems in nomenclature that have not been considered in naming organic polymers. Extension of the rules to inorganic and some semiorganic polymers will therefore require, as a minimum, modifications to permit species not anticipated in the present rules to be named. Moreover, little inorganic chemistry is presented in terms of biradicals, at least in the same sense as in organic chemistry. Consequently, there is no real basis for naming the repeat units of many of these polymers as bivalent radicals.

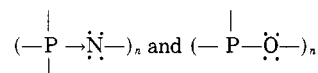
To the present time, very little has been done toward naming inorganic polymers. The 1957 IUPAC rules for

inorganic nomenclature<sup>3</sup> are not basically concerned with polymers. Rule 7.42 for naming extended polynuclear coordination compounds comes closest to a general system for a specific class of inorganic polymers. In it, the name cesium catena- $\mu$ -chloro-dichlorocuprate(II) is suggested for



Catena is used rather than poly, to signify that the polymer has a simple chain structure. Any coordination polymer that has a chain structure obviously can be named in this fashion. Other inorganic polymers have been named on a haphazard basis, if they have been named at all. In addition to names based on the rule just cited, *Chemical Abstracts*, uses a variety of other names, such as phosphonitrile polymers, poly(siloxanes), poly(silylenes), and poly(selenomethylene).

A number of inorganic and semiorganic polymers can be viewed as assemblages of biradicals. Naming them by the tentative rules for organic polymers would pose no problem, were it not for two things. First, in many cases, there are fairly widely used names not based on biradicals, and second, there are no established names for many of the biradicals involved. Consider, for example, poly(siloxanes)  $(\text{---SiRR'---O---})_n$ , poly(silicates)  $[\text{---Si(O}^-\text{)}_2\text{---O---}]_n$ , poly(silazanes)  $(\text{---SiRR'---NR''---})_n$ , poly(phosphazenes) or poly(phosphonitriles)  $(\text{---PRR'---N---})_n$ , poly(phosphates)  $[\text{---P(O)(O}^-\text{)---O---}]_n$ , and poly(stannomethylenes)  $(\text{---SnRR'---CR''R'''---})_n$ . The biradical names poly(oxy- $R, R'$ -silylene), poly( $R, R'$ -imino- $R, R'$ -silylene), and poly( $R, R'$ -stannylene- $R'', R'''$ -methylene) for the first, third, and last of these examples follow from the tentative rules. There is a complication in the case of the fourth and fifth examples. As Adams has noted,<sup>1</sup> the species involved are isosteres insofar as the backbone is concerned, i.e.,



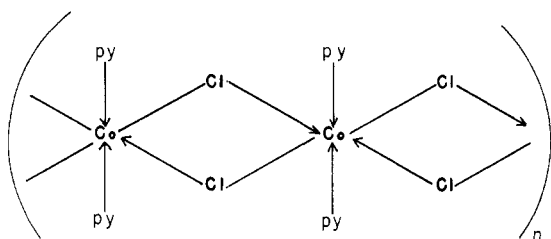
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Which electron pair is drawn as an arrow has no physical significance, of course, although the  $P \rightarrow N$  is generally considered to be a double bond in the backbone of the former and the  $P \rightarrow$  a double bond to a side group in the latter. Since bond orders are arbitrary, perhaps, as Adams suggests, nomenclature should be based on liganey.

Coordination polymers are not as straightforward to name on a biradical basis. In a most general sense, a coordination polymer is a polymer that contains a coordinate covalent bond in its repeat unit. Such a polymer can be inorganic, organic, or semiorganic. Coordination polymers fall into the following broad classes:

1. Those with backbones held together by bridges which form only one bond with a given center.
2. Those with backbones held together by bridges which chelate to one or more centers.
3. Those consisting of polymer ligands which contain donor sites either in the backbone or side chains, to which are bonded coordination centers.
4. Those containing coordination centers in the backbone, to which are bonded ligands as side groups.

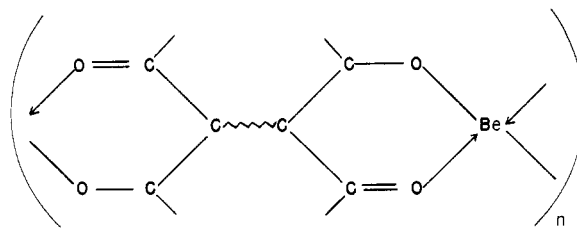
Each class presents nomenclature problems of its own. An example of the first class is the polymeric form of  $\text{Co}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$ ,<sup>4</sup> which can be written



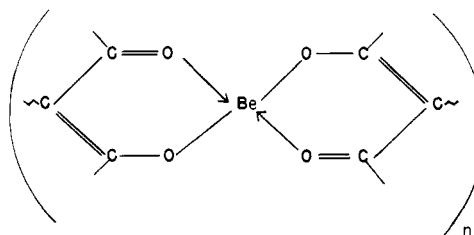
In this structure, there are two simple chloride bridges between each pair of cobalt(II) centers. It is not clear as to whether or not the 1957 rule applies to this polymer, because it does not contain a simple alternating chain of atoms. A possible name is catena-di- $\mu$ -chloro-*trans*-bis(pyridine)cobalt(II). Here, however, the poly(radical) concept breaks down, for the repeat unit is not a radical, but a molecule which exists in its own right as a monomeric tetrahedral isomer of the polymer form. There is no precedent for naming a bridging chloride as a bivalent radical.

A similar situation is found with palladium(II) chloride, except that neither form is monomeric. One is a hexameric cluster of six palladium atoms held together by chloride bridges.<sup>5</sup> Each palladium atom occupies a corner of an octahedron, and the chloride bridges occupy the edges of the octahedron. The polymeric form has double chloride bridges between palladium centers in a configuration equivalent to the backbone of polymeric  $\text{Co}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$ .<sup>4</sup> Both forms can be named as coordination compounds by inorganic nomenclature rules presently under consideration. Again, names based on biradicals have no precedent, even though in this case the hypothetical monomer is found only as an excited species.

The structure of the second kind of coordination polymer cited is usually fairly obvious from the composition. The beryllium(II) derivative of a symmetrical bis- $\beta$ -diketone is probably a linear chain with bischelate bridges between beryllium centers, i.e.,

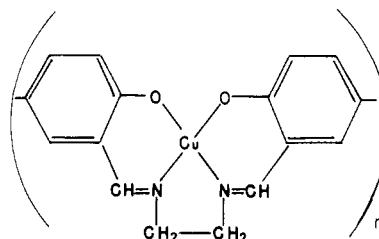


Polymers of this type containing organic bridging groups can be forced into a biradical naming system if the structure is written appropriately, i.e.,

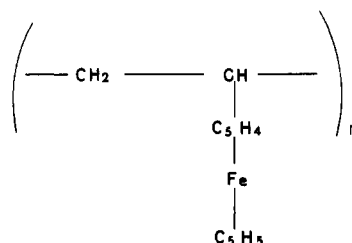


It is then only necessary to coin a name for the biradical that has been chosen as the repeat unit. Coordination chemists will undoubtedly resist such a naming procedure, however, since it ignores the building blocks of the polymer. They would probably be more satisfied with a name showing the bis- $\beta$ -diketonate as a bridging group. It is interesting to note, in this connection, that the polymer  $-\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4-$  is becoming known as poly(ferrocenylene). In this case, a radical name has been derived from the trivial name for the parent polymer.

Presumably, the third kind of coordination polymer offers the fewest problems to naming. One example is the copper derivative of a polymeric Schiff base,

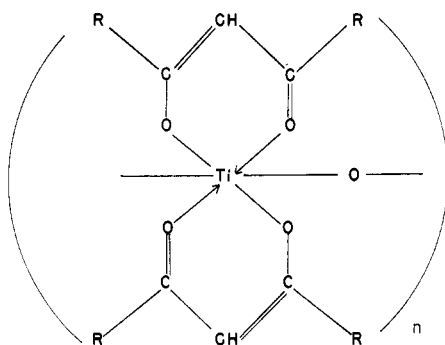


It can be named as the copper derivative of a polymer that can be named by the tentative polymer nomenclature rules. If the donor groups are in a side chain instead of in the backbone, structures such as the following result:



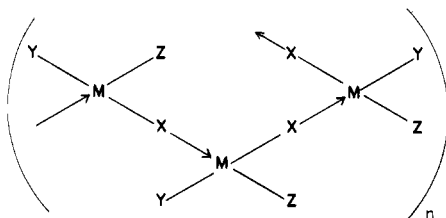
Again, once the polymer ligand is named, the coordination polymer can be named in principle. In this particular case, the side group also can be named as a ferrocenyl

group and the polymer as a ferrocenyl substituted poly(ethylene). An example of the last kind of coordination polymer is

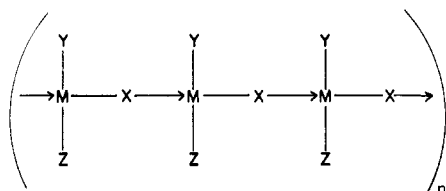


There are no coordinate covalent bonds in its backbone, so in principle, biradical names can be used without choosing artificial repeat units. Since the recommended radical names for metallic elements do not imply oxidation states, current proposals would lead to the name poly[oxy-bis(acylketonato)titanio]. Workers in the field would be more apt to use poly[bis(acylketonato)titanoxane].

Once a system for naming polymers containing non-tetrahedral elements has been devised, the designation of isomerism should be no problem. Consider the isomeric forms possible with a square planar center



and



In this case, the use of *cis* and *trans* would be sufficient to distinguish the two. Thus, the first polymer would be *cis*-catena- $\mu$ -X-YZM and the second *trans*-catena- $\mu$ -X-YZM according to current coordination chemistry usage. A similar pair can be pictured with octahedral centers by adding ligands above and below the planes of the centers. Optical activity is then also possible for the *cis* form. Consequently, there are *d*-, *l*-, and *meso* forms to consider. Once a basic nomenclature system is devised, it should be relatively easy to make provision for such possibilities.

In summary, the simplified picture presented here suggests that there are two broad classes of inorganic polymers. One contains true biradical repeat units and can be named in much the same way as organic polymers, once agreement is reached on how to name the biradicals. The second, however, is not really amenable to a biradical approach. Names for these polymers, all of which contain coordinate covalent bonds in their backbones, can be derived from current coordination chemistry nomenclature. It might be desirable to consider the whole problem of inorganic polymer nomenclature separately, rather than using the organic system where it fits and an alternate system where it does not. Semiorganic polymers would then be named in a fashion appropriate to their chemistry.

#### LITERATURE CITED

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