LA-UR-97-3414

Approved for public release; distribution is unlimited

Title: **Advanced Polymer Chemistry of Organometallic Anions**

Author(s): R. M. Chamberlin, CST-11
K. D. Abney, CST-11
G. J. Balaich, U.S. Air Force Academy
S. A. Fino, U.S. Air Force Academy

Submitted to: DOE Office of Scientific and Technical Information

Los Alamos
NATIONAL LABORATORY

Advanced Polymer Chemistry of Organometallic Anions

Rebecca M. Chamberlin* and Kent D. Abney
Los Alamos National Laboratory

Gary J. Balaich and Steve A. Fino
United States Air Force Academy

Abstract

This is the final report of a one-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The objective of the project was to prepare and characterize new polymers incorporating cobalt dicarbollide. Specific goals were to prepare polymerizable cobalt dicarbollide monomers using the nucleophilic substitution route discovered in our laboratories and to establish the reaction conditions required to form polymers from these complexes. This one-year project resulted in two publications (in press), and provided the foundation for further investigations into polymer synthesis and characterization using cobalt dicarbollide and other metallocarboranes.

Background and Research Objectives

Transition metal complexes have important utility as monomer units in polymer chains because they ultimately determine the unique electronic, optical, and catalytic properties of the polymer.[1] Our interest in synthesizing organometallic polymers containing the cobalt bis(dicarbollide) anion is motivated by their possible application as cation exchange materials for the remediation of cesium-137 and strontium-90 from nuclear wastes.[2] Cobalt dicarbollide can be used to selectively extract cesium and strontium when used in a solvent extraction mode, but it has never been incorporated into an effective ion exchange resin. Polymers with cobalt dicarbollide in their backbone should have a large inherent ion exchange capacity and potentially be equally selective for cesium and strontium.

We are therefore directing work at the synthesis and characterization of polymeric materials that incorporate cobalt dicarbollide in the main polymer chain. Our initial efforts focused on attaching organic functional groups at the carbon sites of cobalt dicarbollide to produce derivatives with reactivity towards addition and condensation polymerization. Although a few polymers containing metallocarborane groups have been reported,[3] no

* Principal Investigator, E-mail: rlmiller@lanl.gov

example of a polymer containing the metal (bis)dicarbollide group in the main chain has yet appeared.

Importance to LANL's Science and Technology Base and National R&D Needs

Improved ion-exchange technologies are urgently needed for high-level nuclear-waste pretreatment, plume characterization, monitoring and remediation of contaminated soils and waters, and decontamination and decommissioning activities. In all these examples, radioactive cesium, strontium, barium and radium must be monitored, separated, and disposed of in an environmentally benign manner. Polymers containing weakly coordinating metal dicarbollide anions are expected to selectively take up these low-valent cations for applications in chemical sensing and separations. The chemical inertness of cobalt dicarbollide makes it ideal for use in boron neutron capture therapy, an emerging method in cancer radiotherapy.[4] This work will provide methods for attaching cobalt dicarbollide to polymers or antibodies for medical uses. Cobalt dicarbollide has also been used as a noncoordinating anion in homogeneous catalysis.[5] Using methods developed through this research, it will be possible to immobilize the anion on a support, facilitating product separation and catalyst recovery. Thus, this multidisciplinary project will advance fundamental polymer science and solve real national and international problems.

Scientific Approach and Accomplishments

Cobalt dicarbollide, $Cs[Co(C_2B_9H_{11})_2]$, was selectively deprotonated at one or two of its carbon atoms using the strong base reagent, butyllithium. The products of this reaction are purple $[Co(LiC_2B_9H_{10})(C_2B_9H_{11})]$ (**1**) and blue $[Co(LiC_2B_9H_{10})_2]$ (**2**), respectively. Both of these lithio(cobalt dicarbollide) complexes can be isolated as crystalline solids, or used immediately in typical nucleophilic substitution reactions. For this project, **1** and **2** were treated with dry carbon dioxide gas to form the carboxylic acid anions, $[Co(C_2B_9H_{11})(C_2B_9H_{10})(COOH)]^-$ (**3**) and $[Co(C_2B_9H_{10})_2(COOH)_2]^-$ (**4**). Acids **3** and **4** are air-stable red solids that dissolve in dilute aqueous bases and in organic solvents such as THF and acetone. Both were characterized by their infrared spectra, which showed strong absorbances at 3099-3730 cm^{-1} and 1704 cm^{-1} that are typical of carboxylic acids, as well as strong B-H stretching vibrations at 2556 cm^{-1}. Additional

characterization by NMR and combustion elemental analysis confirmed this characterization.

Compounds **3** and **4** show reactivity typical of organic carboxylic acids, including reaction of **4** with thionyl chloride ($SOCl_2$) to form a di(acidchloride), $[Co(C_2B_9H_{10})_2(COCl)_2]$ (**5**) (See Scheme in Fig. 1). Di(acid chlorides) are highly reactive toward amines, and are routinely used to prepare polyamides such as Nylon. We found that di(acid chloride) compound **5** does react with amines and diamines. For example, the reaction between **5** and hexamethylenediamine, the amine used to make Nylon-66, quickly forms a brown solid that dissolves in DMSO but in few other solvents. Characterization data for this product is consistent with the polymer formulation shown in the Scheme (Fig. 1). Key features of the infrared spectrum are the amide-type absorptions at 3417, 3268, 3046 and 1526 cm^{-1} (the amide NH bonds) and 1636 cm^{-1} (the amide CO bond).

Dicarboxylic acid **4** also reacts with amines. As shown in the Scheme (Fig. 1), the acid (**4**) reacts at room temperature with the weak base hexamethylenediamine to precipitate a red complex salt, $[Co(C_2B_9H_{10})_2(COO^-)_2(^+H_3N(CH_2)_6NH_3^+)]$ (**7**). Prominent features in the infrared spectrum of compound **7** include bending and stretching bands at 1583 and 1352 cm^{-1}. Forming the salt is advantageous because it ensures that the polymer will be formed from an exact 1:1 mixture of the acid and amine, thus maximizing the chain length of the individual polymer strands.

Polymerization of **7** occurs by thermal conversion, which is shown in Fig. 2. The thermogravimetric analyzer (TGA) trace at the top shows the weight of the material as it is heated. The first sharp weight loss occurs when adsorbed solvent (THF) is vaporized. The second region of weight loss corresponds to the formation and vaporization of water as the polymer forms. The lower trace in Fig. 2 is from the Differential Thermal Analyzer (DTA), which measures the heat energy released or absorbed from the sample as chemical reactions occur. The sharp drop occurs after about 10 minutes of heating because volatilization of THF requires heat energy to be absorbed by the sample. However, at 30 minutes there is a sharp rise in the DTA trace, indicating that the polymerization reaction is releasing heat energy, as expected.

By preparing the polyamide using two different chemical reactions, we have shown that carboxylic acid derivatives of cobalt dicarbollide can be potentially incorporated into a vast number of polymeric materials such as polyesters, polyurethanes and polybenzimidazoles. The chemical and physical properties of polymers containing cobalt dicarbollide will be investigated further at the U.S. Air Force Academy, supported by funding from the Air Force Office of Scientific Research. Funding will be sought from the

Environmental Management Program Office of DOE in order to develop the ion exchange applications of these polymers at LANL.

Publications

1. Chamberlin, R.M.; Scott, B.L.; Melo, M.M.; Abney, K.D. "Butyllithium Deprotonation versus Alkali Metal Reduction of Cobalt Dicarbollide: A New Route to C-Substituted Derivatives." *Inorg. Chem.*, in press.

2. Balaich, G.J.; Fino, S.A.; Chamberlin, R.M.; Abney, K.D. "Synthesis of an Organometallic Polyamide of Cobalt Dicarbollide." *Inorg. Chem.*, submitted.

References

[1] Pittman, C.U., Jr.; Carraher, C.E., Jr.; Zeldin, M.; Sheats, J.E.; Culbertson, B.M., eds., Metal-Containing Polymeric Materials, New York: Plenum Press, 1996.

[2] Miller, R.L.; Pinkerton, A.B.; Hurlburt, P.K.; Abney, K.D., Solv. *Extr. Ion Exch.*, **13**, 813 (1995). Fanning, J.C.; Huff, L.A.; Smith, W.A.; Terrell, A.S.; Yasinsac, L.; Todd, L.J.; Jasper, S.A.; McCabe, D.J., *Polyhedron*, **14**, 2893, (1995). Kyrs, M.; Alexova, J., *J. Radioanal. Nucl. Chem. Letters*, **187**, 285 (1994). Kyrs, M.; Selucky, P.; *J. Radioanal. Nucl. Chem.*, **172**, 213 (1993).

[3] Kats, G.A.; Komarova, L.G.; Rusanov, A.L., *Vysokomol. Soedin., Ser. B*, **34**, 62 (1992). Zakharkin, L.I.; Kats, G.A.; Komarova, L.G., *Plast. Massy*, **11**, 61 (1990). Chandrasekaran, E.S.; Thompson, E.A.; Rudolph, R.W., *Inorg. Chem.*, **17**, 760 (1978).

[4] Moody, D.C.; Peterson, E.J., eds. "Proceedings of the DOE Workshop on the Role of a High-Current Accelerator in the Future of Nuclear Medicine." Los Alamos National Laboratory report LA-11579-C (1989).

[5] Yang, X.; King, W.A.; Sabat, M.; Marks, T.J., *Organometallics*, **12**, 4254 (1993). Hlatky, G.G.; Eckman, R.R.; Turner, H.W., *Organometallics*, **11**, 1413 (1992). Grossman, R.B.; Doyle, R.A.; Buchwald, S.L., *Organometallics*, **10**, 1501 (1991).

SCHEME

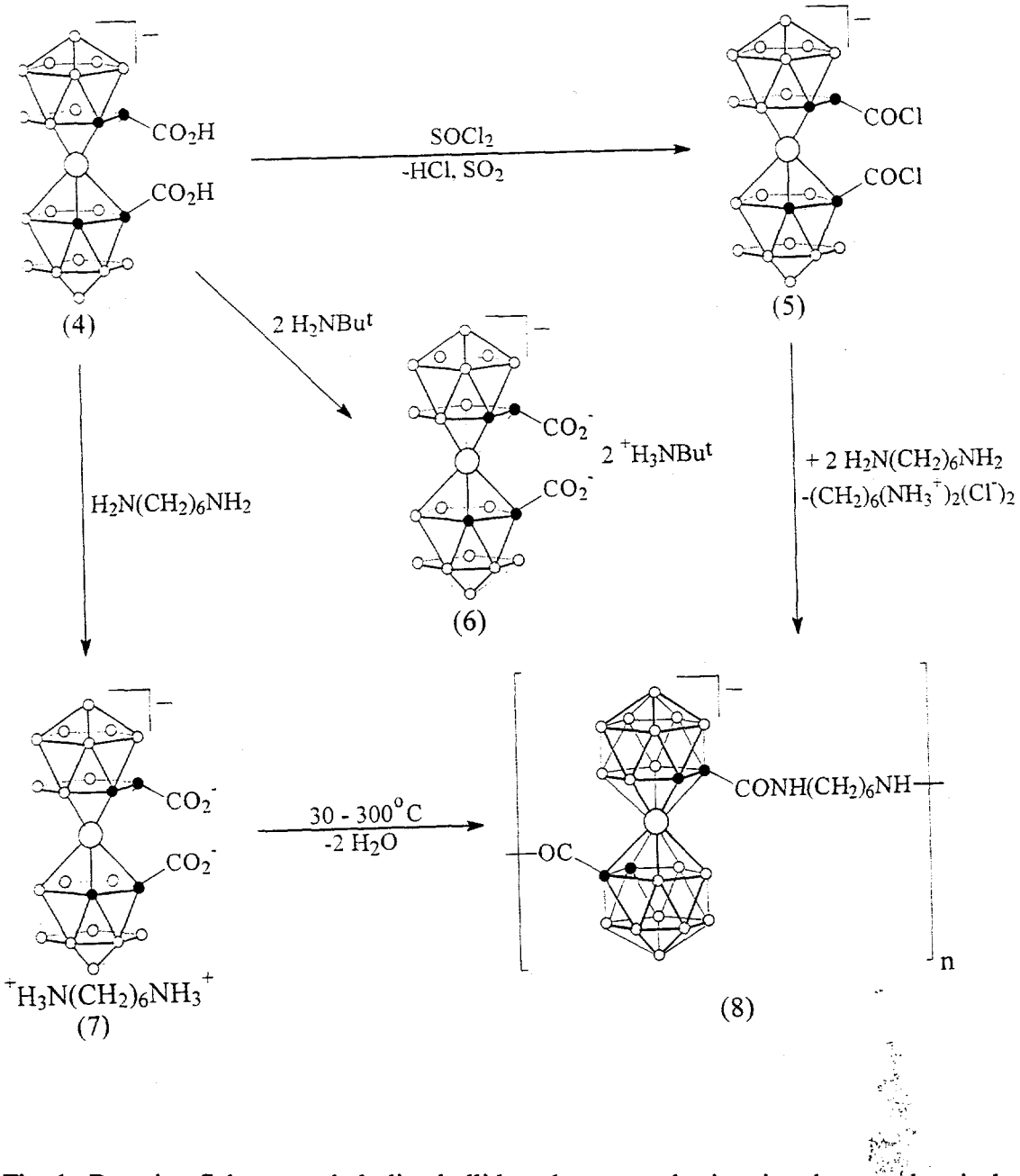

Fig. 1. Reaction Scheme: cobalt dicarbollide polymer synthesis using the two chemical routes described in the text.

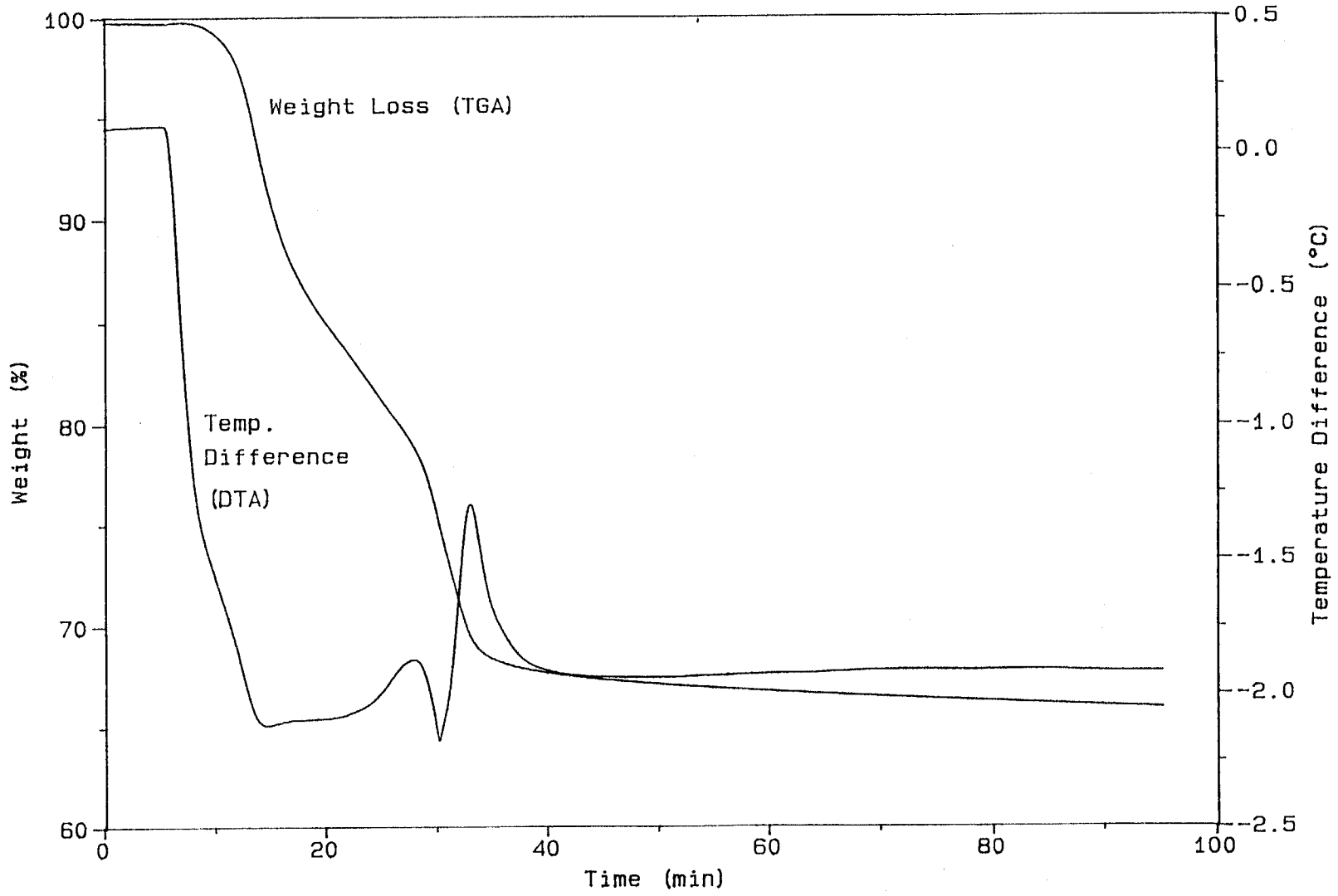

Fig. 2. Weight loss and energy absorption by complex salt **7** during thermal formation of the cobalt dicarbollide–polyamide.