Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Metal Salts and Complexes as Structural Models and Templates for The Solid State Polymerization of Substituted Acetylenes

Bruce M. Foxman [a] & J. D. Jaufmann [a]

[a] Department of Chemistry, Brandeis University Waltham, MA, 02254, U.S.A.

Version of record first published: 20 Apr 2011.

To cite this article: Bruce M. Foxman & J. D. Jaufmann (1984): Metal Salts and Complexes as Structural Models and Templates for The Solid State Polymerization of Substituted Acetylenes, Molecular Crystals and Liquid Crystals, 106:3-4, 187-197

To link to this article: http://dx.doi.org/10.1080/00268948408071443

Mol. Cryst. Liq. Cryst., 1984, Vol. 106, pp. 187-197
0026-8941/84/1064-0187/$18.50/0

METAL SALTS AND COMPLEXES AS STRUCTURAL MODELS AND TEMPLATES FOR THE SOLID STATE POLYMERIZATION OF SUBSTITUTED ACETYLENES

BRUCE M. FOXMAN and J. D. JAUFMANN
Department of Chemistry, Brandeis University
Waltham, MA 02254, U.S.A.

Abstract In an extensive study of the preparation and solid-state reactivity of transition metal phosphine complexes it was found that nearest-neighbor interactions, nucleation, temperature, doping, polymorphism and crystal symmetry greatly influenced the course of the thermal solid state reactions. With the perspective of the solid state chemistry developed by Morawetz and Schmidt, the principles and techniques developed in our laboratory have been applied to the radiation-induced solid state polymerization of metal alkynoate complexes, leading to the first rationally designed synthesis of substituted polyacetylenes in the solid state. The structural principles which led to this synthesis are described herein. The reactivity of several different monomer phases is contrasted in the context of crystal structure, metal electronic structure and radiation sensitivity.

Our recent research efforts have concentrated on studies of monomeric transition metal complexes of the general formula NiX_2L_2 (X = Cl, Br, I, NCS; L = $P(CH_2CH_2CN)_3$) which undergo single-crystal coordination polymerization reactions.[1-5] In these reactions square planar monomer is smoothly transformed to octahedral polymer (via bridging nitrile groups) in the solid state; the reactions are characterized by chemical and crystallographic specificity, stereodirectionality, highly anisotropic "front motion" in single crystals, and reversibility. Comparative studies of complexes with subtle chemical (substitutional or doping) differences led to a series of guidelines for understanding, predicting and controlling the solid-state reactivity of the materials.[5] We were able to draw important conclusions for these thermal solid state reactions regarding the influence of nearest-neighbor interactions, nucleation, crystal symmetry and polymorphism on reactivity.[5]

Given the foregoing results, we felt it desirable as a next step to devise a general scheme for the polymerization of vinyl and acetylenic monomers in the solid state, using metal complexes as a "basis" for controlling both structure and reactivity. The influence of the crystal lattice on the radiation-induced solid state polymerization of metal acrylate salts, acrylamide and other vinyl monomers was discussed in the literature as early as 1956.[6] These ideas were developed more fully in the next ten years through a series of elegant experiments conducted by Professor Herbert Morawetz[7] and coworkers at the Polytechnic Institute of Brooklyn and by Professor Gerhard Schmidt and collaborators at the Weizmann Institute of Science.[8]

Our initial ideas, then, were a logical extension of all of the above work in the context of Schmidt's "topochemical postulate": i.e., for α,β-unsaturated carboxylic acids, centers capable of undergoing stereospecific (2+2) photocycloaddition in the solid state must be oriented parallel to one another and at distances $\leqslant \sim 4.0Å$. Such contacts characterize the reactive phases of cinnamic acid[8] and 2,5-distyrylpyrazine[9] which dimerize and polymerize respectively by photocycloaddition processes. Examination of the structural literature suggested that several forms of saturated carboxylate-metal complexes and salts had packing arrangements reminiscent of those of the cinnamic acids, and thus their unsaturated analogues might be expected to undergo solid-state polymerization.

In order to test this idea, it was first necessary to find a potential metal (saturated-carboxylate) "model structure" with relatively short C-C contacts, and then to prepare a nearly isomorphous unsaturated analogue where the pendant organic moieties made an approach which might allow for a reaction to occur. Owing to the change in carbon atom stereochemistry with degree of saturation, it was of course impossible to find a complex which would exhibit strict molecular isosterism[10] with an unsaturated analogue. However, we reasoned that there was sufficient structural similarity betweeen acetic acid and its linear structural analogue, propiolic acid, H-C≡C-COOH, to provide a suitable test of the idea. The crystal structure of bis(acetato)tetraaquonickel (II)[11] seemed an excellent choice (see Figure 1) as there were $H_3C\cdots CH_3$ contacts of $\sim 3.9Å$. Thus, bis(propiolato)tetraaquonickel(II), -cobalt(II) and -zinc(II) were prepared and found to be isomorphous (Ni, Co, Zn). Further, these materials exhibited a similar diffraction pattern to the acetate analogue. The crystal structure (Figure 2) shows the great similarity in packing, and the short contacts observed between molecules. The nickel, zinc and cobalt propiolate crystals react under x- or γ-irradiation to yield amorphous brown-black metal polypropiolates,[12] which are easily separated from residual monomer. We have now synthesized a large number of metal propiolate salts and complexes, and several patterns are beginning to emerge, viz.,

1. New structure types, involving unusual metal and/or carboxylate coordinatation, characterize the inorganic structural chemistry of these materials.
2. Crystal structures involving both the shortest C-C intermolecular interactions and translationally-related reactants show the highest reactivity, yield and purity of polymeric product (see Figure 3 - - anhydrous sodium propiolate).
3. Structures containing reactive and unreactive propiolate groups (based on distance criteria) produce (upon γ-irradation) polymeric products which also contain unreacted, monomeric propiolates.
4. Isomorphous phases may show differing reactivity, e.g., for $M(H_2O)_4\ (O_2C\text{-}C \equiv CH)_2$, the M=Co and Ni phases are relatively unreactive, while high reactivity is observed for M=Zn. Further, the M=Ni and Co complexes explode upon heating, while the isomorphous Zn phase

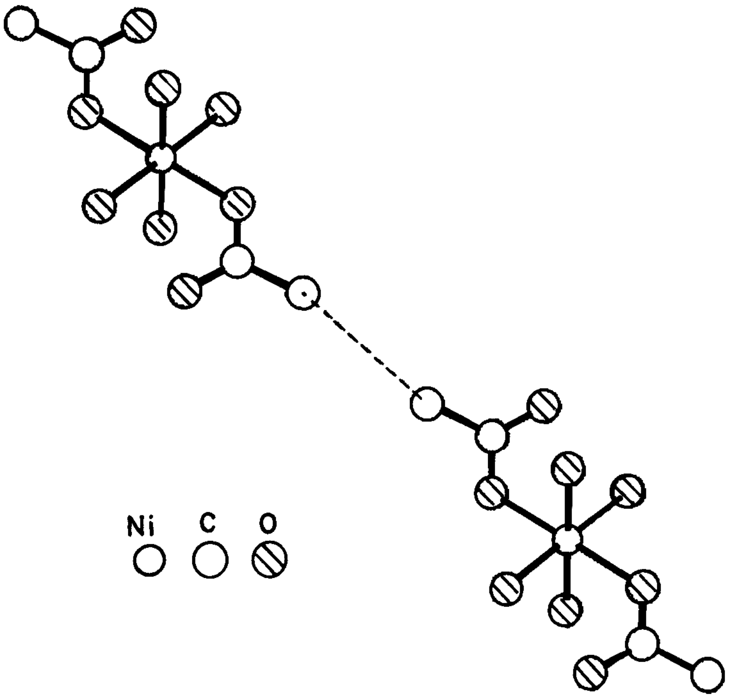

Figure 1. Two molecules of tetraaquonickel (II) acetate showing a short CH_3-CH_3 contact of ~ 3.9Å (drawn by ORTEP using data from reference 11).

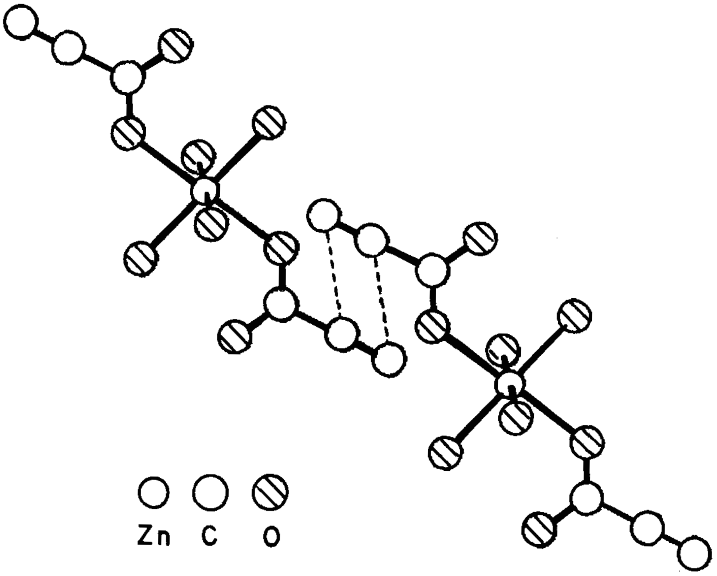

Figure 2. Two molecules of tetraaquozinc (II) propiolate showing the rather similar packing arrangement to that in Figure 1. Overlap of the acetylenic moieties leads to short contacts of 3.4-3.5Å in this reactive phase. The analogous nickel and cobalt phases are isomorphous.

simply melts. We believe these phenomena to be related to certain redox processes in these solids, and experiments are in progress to test these ideas. Doping of different metals into a host phase might be expected to alter the reactivity of the host, which is also under investigation.

5. The conjugated polymers obtained from various monomer phases have properties directly related to the monomer structure. Thus, the structure-type determines the nature of the polymer; the metal serves only to control the rate of reaction, either as in item 4 above, or by altering the absorption cross section of the sample for the incident radiation. The reactivity of a given material thus results from a balance of at least three important factors: (i) structural criteria, i.e. nearest-neighbor distances; (ii) the influence of the metal on radical stability and/or decarboxylation with concomitant production of a metal acetylide; and (iii) the relative absorption (as the metal is varied) of the incident radiation by the sample. These criteria provide a means of controlling and tailoring the reactivity of various monomer phases.

This project has a series of long-term goals; these include: (i) the development of new structure types at the molecular and crystal level; (ii) development of structure-reactivity relationships for polymerizable monomer phases; (iii) production of

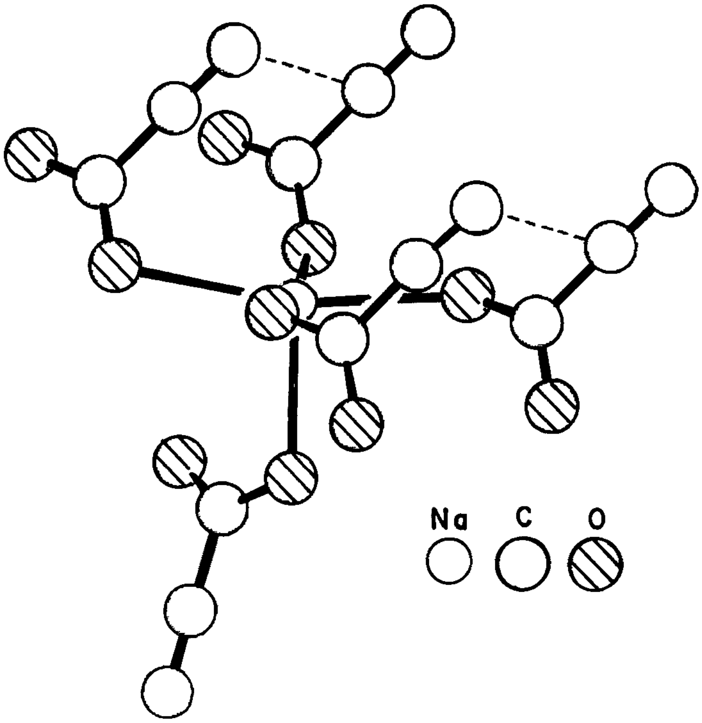

Figure 3. Structure of Sodium Propiolate. Dashed lines indicate short 1,2 contacts (3.29Å) between reactive acetylenic centers.

high-crystallinity polymers; (iv) production of new amorphous or crystalline polymers (or coordination polymers) with unusual properties; (v) development of applications for appropriate materials. At this time areas (i), (ii) and (iv) are under active study. A pseudopolymorph[13] of hydrated calcium acrylate shows considerable promise as a precursor for the production of highly oriented polyacrylates, and similar experiments are underway with new propiolate phases.

This research was supported in part by the Office of Naval Research.

REFERENCES

1. K. Cheng and B. M. Foxman, J. Am. Chem. Soc., 99, 8102 (1977).
2. K. Cheng, B. M. Foxman and S. W. Gersten, Mol. Cryst. Liq. Cryst., 52, 77 (1979).
3. B. M. Foxman and S. W. Gersten, Inorg. Chim. Acta, 33, L151 (1979).
4. B. M. Foxman, P. L. Goldberg and H. Mazurek, Inorg. Chem., 20, 4368 (1981).
5. B. M. Foxman and J. D. Jaufmann, J. Polym. Sci., Sect. C, 70, 31 (1983).
6. A. J. Restaino, R. B. Mesrobian, H. Morawetz, D. S. Ballantine, G. J. Dienes and D. J. Metz, J. Am. Chem. Soc., 78, 2939 (1956).
7. Representative papers include: (a) Reference 6; (b) H. Morawetz and I. D. Rubin, J. Polym. Sci., 57, 669, 687 (1962); (c) J. B. Lando and H. Morawetz, J. Polym. Sci., Sect. C., 4, 789 (1964); (d) H. Morawetz, J. Polym. Sci., Sect. C., 12, 79 (1966).
8. (a) M. D. Cohen and G. M. J. Schmidt, J. Chem. Soc., 1996 (1964); (b) F. L. Hirshfeld and G. M. J. Schmidt, J. Polym. Sci., Sect. A, 2, 2181 (1964); (c) M. D. Cohen and B. S. Green, Chem. Brit., 9, 490 (1973) and references therein.
9. H.-G. Braun and G. Wegner, Mol. Cryst. Liq. Cryst., 96, 121 (1983) and references therein.

10. J. Z. Gougoutas, W. H. Ojala, C. R. Ojala and P. J. Fritz, Abstr. 17th Great Lakes Regional Meeting, American Chemical Society, June 1983, Abstract 36.

11. J. N. van Niekerk and F. R. L. Schoening, Acta Cryst., 6, 609 (1953).

12. B. E. Davidov, B. A. Krentsel and G. V. Kchutareva, J. Polym. Sci., Sect. C, 16, 1365 (1967).

13. C. A. Booth and B. M. Foxman, to be published.