Structure and Solid State Reaction of Tris(propynoato)scandium(III), an Unusual Coordination Polymer

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Irradiation (^{60}Co γ-rays) of the novel, cubic three-dimensional coordination polymer, tris(propynoato)scandium(III), induces a solid-state polymerization reaction; analysis of the structure indicates that the criterion of parallelism is not a necessary requirement for the reactivity of monoacetylenes in solids.

Metal carboxylates have played, and continue to play, an important role in the development of coordination chemistry.[1] However, until the last decade, the use of unsaturated carboxylate ions as ligands had been little explored. Recent studies of metal complexes of unsaturated carboxylates have led to (*i*) new and unanticipated coordination polymers and oligomers,[2] and (*ii*) the development of rational syntheses of mixed metal complexes.[3] The presence of pendant unsaturated groups in metal carboxylates provides a set of reactive centres which may be proximate in the solid state. In such an exemplary case, a set of 'favourable' intermolecular contacts will satisfy the criteria for the onset of solid state reactivity.[4] As an example, we have demonstrated that crystalline metal salts of propynoic acid polymerize readily upon irradiation with UV light or ^{60}Co γ-rays.[5] The ready availability of single crystals of many of these materials has allowed us to develop structural criteria for the reactions of monoacetylenes in the solid state.[5,6] Since the maturation of our understanding of solid state reactivity depends upon the establishment of a reliable structural database of reactive complexes and salts, *we have extended* our studies to trivalent metal ions. This communication reports the preparation and structure of a new type of coordination polymer and its behaviour upon γ-irradiation.

Tris(propynoato)scandium(III) **1** is prepared readily by the slow addition of solid scandium carbonate to a stirred aqueous solution of propynoic acid. Evaporation of the resulting solution gave colourless cubic crystals of **1**. Solid **1** is an extremely hard substance; on that basis we suspected a polymeric structure. An X-ray structure determination† of **1** showed that the complex had the expected octahedral geometry (Fig. 1), with the propynoate ligands bridging pairs of Sc atoms in an *anti–anti* fashion. The cubic unit cell contains two symmetry-independent Sc atoms, each occupying a site of crystallographic $\bar{3}(S_6)$ symmetry, but only one independent propynoate ligand; the configuration about each Sc atom is nearly identical. A stereoview of the unit cell (Fig. 2) reveals that each Sc atom is bridged to six other Sc atoms. This leads to an infinite, cubic, three-dimensional coordination polymer, an unprecedented structure for a metal(III) carboxylate. As a result of the relatively large Sc–O–C angles (average 151.1°), all interatomic vectors except those for C–O bonds lie nearly parallel to the unit cell edges. By contrast, tris(acetato)scandium(III) has a linear polymeric structure with the carboxylate ligand again bridging pairs of scandium atoms; however, the bridging occurs in a *syn–syn* fashion, leading to an infinite one-dimensional coordination polymer.[7] Tris(formato)scandium(III) is a distorted three-dimensional coordination polymer, with *anti–anti* and *syn–anti* bridges between Sc atoms.[8]

As observed in other solid-state polymerization reactions of metal propynoates, solid **1** develops a deep-orange colour upon ^{60}Co γ-irradiation.[5,6] As the irradiation proceeds there is a concomitant loss in intensity of the –C≡C– stretching mode at 2110 cm^{-1}, indicating probable formation of a polypropynoate.[9] Conversion to product occurs linearly with time; yields of *ca.* 55% are obtained after 40 Mrad doses. The amorphous product is isolated after removal of reactant by extraction with water. The product is slightly soluble in D_2O–DCl solution, and ^{1}H and ^{13}C NMR spectra of the product consist of broad resonances too poorly resolved to allow assignment of the possible stereochemistry of the product(s). However, the resonances lie in the regions expected for a polypropynoate species or a substituted polyacetylene (^{1}H, δ 6–8; ^{13}C, δ 120–140, 160–175).[5,6,10]

This work points out an important difference between the structural criteria for the reactions of alkenes and alkynes in the solid state. For alkenes, distance (groups separated by ≤4.2 Å) and parallelism requirements are usually met.[4,11] Earlier work[5,6] has demonstrated that solid state polymerization of propynoates will occur if there are infinite chains of short –C≡C–···–C≡C– contacts ≤4.2 Å; these contacts usually occur between parallel or nearly parallel acetylene moieties. In the present case the only repeating chains of short acetylene–acetylene contacts are between nearly orthogonal acetylenes (Fig. 2). There are two infinite sets of –C≡C–··· –C≡C– contacts, C(2)–C(3) [*z,x,y*], 3.79 Å and C(2)–C(3) [1/2 – *z,x* – 1/2, *y*], 4.02 Å. Thus, the criterion of parallelism is not a necessary requirement for the reactivity of monoacetylenes in solids.

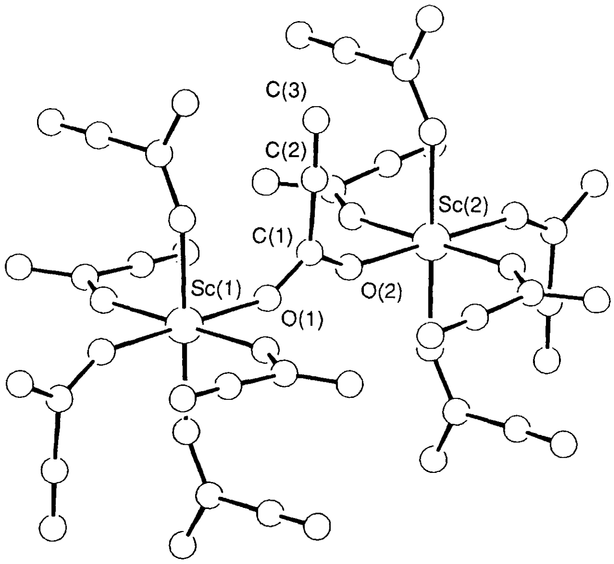

Fig. 1 Two molecules of **1** showing the *anti–anti* bridging arrangement of the propynoate ligand. Selected bond distances and angles include: Sc(1)–O(1), 2.091(2); Sc(2)–O(2), 2.081(2) Å; Sc–O(1)–C(1), 150.8(2); Sc(1)–O(2)–C(2), 151.7(2); Sc(1)–O(1)–O(2), 176.0(1); Sc(2)–O(2)–O(1), 175.6(1)°.

In order to obtain further information about the solid state reaction we collected two additional sets of X-ray diffraction data on the crystal used in the structure determination. Prior to each of these two experiments, we irradiated the crystal with ^{60}Co γ-rays (16 Mrad dose). As expected for a material converting from a single crystal to an amorphous solid, the intensities of all reflections gradually decrease, with those due primarily to the propynoate ligands decreasing more rapidly. In both experiments, atomic displacement parameters increased markedly, particularly those of the carbon atoms. Seiler and Dunitz[12] noted that the changes in an X-irradiated crystal (increases in atomic displacement parameters and cell parameters) were similar to those observed for a thermal expansion. However, there is a striking difference apparent in the present study. After the two 16 Mrad doses of ^{60}Co γ-rays, the unit cell constant, *a*, decreased from 12.735(4) to 12.623(5) Å. Such a decrease could arise, for example, from strain exerted upon the reactant lattice by the product phase. In solid acrylamide, potentially reactive molecules make their closest approach along the *b* axis, which decreases[13] during irradiation. The *a* and *c* dimensions for acrylamide increase; a similar effect does not occur in **1** owing to the isotropic distribution of the short contacts. These observations suggest that if topochemical effects influence a radiation-induced reaction/decomposition of a solid, these effects may leave their trace in the change(s) observed in cell constants as the reaction proceeds. Such a phenomenon provides a previously unrecognized opportunity to gain additional geometrical mechanistic information on solids undergoing a transformation from a single crystal to an amorphous solid.[14] In this context it should

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† *Crystal data* for **1**: $C_9H_3O_6Sc$, $M = 252.1$, cubic, space group $Pa\bar{3}$, $a = 12.735(4)$ Å, $U = 2065.4$ Å^3, $Z = 8$, $D_c = 1.622$ g cm^{-3}, $D = 1.64(2)$ g cm^{-3}, μ(Mo-Kα) = 7.17 cm^{-1}. Data were collected at room temperature on a Syntex P2$_1$ diffractometer with monochromated Mo-Kα radiation. The data were corrected for Lorentz-polarization, extinction and absorption effects. Owing to the highly pseudosymmetric nature of the structure, it was necessary to carry out full-matrix least-squares refinement using all 928 unique data and 63 parameters. The structure analysis was further complicated by an orientational disorder (10%) of the propynoate C atoms. The refinement converged to $R = 0.0871$, $R_w = 0.0442$; a structure factor calculation using 301 data for which $I > 1.96\sigma(I)$ led to $R = 0.0291$, $R_w = 0.0251$. Atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

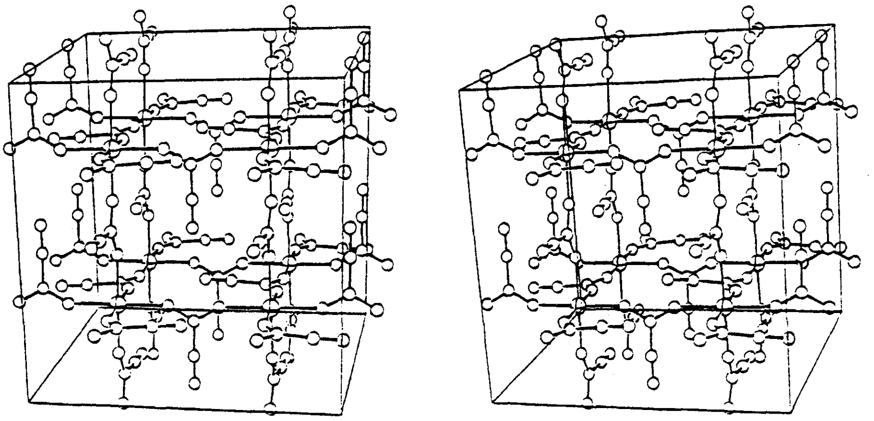

Fig. 2 Stereoscopic view of the crystal structure of **1**. To improve clarity, the unit cell boundaries are drawn from *a*/4 to 5*a*/4.

be useful, in studies of reacting solids, to re-determine the cell parameters at the end of an X-ray data collection if there is evidence of crystal instability upon X-ray exposure.

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