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Preliminary communication

MERCAPTO POLYMER OF BIS-η-CYCLOPENTADIENYLNIOBIUM

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Summary

The preparation of the polymer $\text{-}\!(p\text{-SC}_6\text{H}_4\text{SNb}(\eta\text{-Cp})_2\text{-})_x$, and some of its properties including electrical resistivity, thermal stability and the results of an examination by electron microscopy, are described.

Organometallic polymers are of interest since incorporation of metal atoms into the polymer chain can lead to effects such as catalysis, improved stability, biological activity and novel electrical behaviour [1]. Here, the preparation and some properties of the polymer $\text{-}\!(p\text{-SC}_6\text{H}_4\text{SNb}(\eta\text{-Cp})_2\text{-})_x$ (I) are described. Whole chain resonance is conceivable for this structure and other polymeric mercapto complexes of transition metals where this is so have been found to be highly electrically conducting [2].

A fourfold excess by moles of 1,4-dimercaptobenzene [3] was treated with sodium in ethanol to give a pale yellow solution. To this was added $(\eta\text{-Cp})_2\text{NbCl}_2$ (slight excess over moles of Na) which resulted in a red solution after reaction for 4 h at 60° C. The solvent was removed under vacuum and the residue was repeatedly extracted with dichloromethane to give a deep claret-coloured solution. Addition of petroleum ether resulted in a dark maroon non-crystalline precipitate together with shiny metal-like ribbons attached at right angles to the walls of the vessel. Satisfactory elemental analysis was obtained (Found: C, 53.11; H, 3.93. I calcd.: C, 52.90; H, 3.88%). The mass spectrum shows similarities to that of $(\eta\text{-Cp})_2\text{Nb(SPh)}_2$ [4]. The polymer decomposes above 150° C without melting. It steadily decomposes in solvents in which it is soluble (DMF, DMSO, MeNO_2). This has so far precluded determination of the molecular weight by VPO. For the same reason an ESR spectrum has not yet been obtained but this should be of particular interest since Nb is formally in the +IV oxidation state and should therefore

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possess an unpaired electron. There may be interaction of the unpaired electrons along the polymer chain.

The IR spectrum, otherwise similar to that of $(\eta\text{-Cp})_2\mathrm{Nb(SPh)_2}$ [4], showed a small additional band at 2540 cm^{-1} which can be ascribed to ν(S—H). This indicates the presence of some $\mathrm{C_6H_4SH}$ groups, probably occurring at chain ends. The excess by moles of $p\text{-}\mathrm{C_6H_4(SH)_2}$ over Na in the reaction mixture would have made this likely. The elemental analysis suggests that Cl end-groups are unimportant and that the polymer is of high molecular weight. Its non-crystalline nature, at least for the amorphous material, is also consistent with high molecular weight. EDS analysis (see below) confirms the absence of Cl end-groups for the amorphous material and indicates 2—5% Cl for the ribbons.

In order to try to avoid the presence of SH groups in the starting materials, reaction in DMF of the stoichiometric quantities of $p\text{-}\mathrm{C_6H_4(SNa)_2}$ and $(\eta\text{-Cp})_2\mathrm{NbCl_2}$ has been attempted. However, isolation of the polymeric product was precluded by its decomposition in this solvent.

I was examined by both transmission and scanning electron microscopy. In spite of being uncoated, the samples showed no movement under the electron beam and this indicates that the material is a good conductor. There was no visible damage to the polymer even with an accelerating voltage of 100 kV. Under the transmission microscope, a diffraction pattern of spots was observed for the ribbons but it disappeared within a few seconds. This indicates that there is crystalline order in the ribbons but that rearrangement and/or decomposition occurs under the electron beam. The scanning electron microscope showed the ribbons to be metal-like and of dimensions ca. 0.4 × 0.04 mm with a thickness of 0.1—0.2 μm. EDS analysis indicated that the ribbons and amorphous material have similar chemical compositions (the S peak partly overlaps with the main Nb peak), the only difference being a Cl shoulder in the case of the ribbons, corresponding to 2—5% Cl. Thus, the ribbons may be oligomers with some detectable Cl end-groups, whereas the amorphous material may be higher molecular weight polymer for which the end-groups are not so important. This would explain why the ribbons appeared some time after the amorphous material was first precipitated, since lower molecular weight material is the more soluble. The upper figure of ca. 5% Cl for the ribbons suggests compositions $\mathrm{ClNb}(\eta\text{-Cp})_2\text{-}(\mathrm{SC_6H_4SNb}(\eta\text{-Cp})_2\text{-})_3\mathrm{Cl}$ (M.W. 1384) or $\mathrm{H}\text{-}(\mathrm{SC_6H_4SNb}(\eta\text{-Cp})_2\text{-})_2\mathrm{Cl}$ (M.W. 763). It should be noted that in the case of the preparation of bis-η-cyclopentadienyl Group IVA polyoximes, mechanical agitation was observed to result in the formation of fibres of length $\leqslant$ 1 cm and diameter 10^{-5}—10^{-7} cm [5].

The electrical resistivity of a finely ground sample of I compressed into a pellet was determined by a method similar to that described [6]. Electrical contact was made by means of Ag paste. The resistivity was found to be of the order of 10^{10} Ω cm which is just at the upper limit of the semi-conductor range and similar to that found for many organometallic polymers [7]. The variation of resistivity with applied voltage was low as was observed previously for organometallic polymers [7]. Although whole-chain resonance may be envisaged for I, it should be noted that in the case of the bis-η-cyclopentadienyl Group IVA polyoximes, there was found to be little difference in electrical resistivity between those capable of exhibiting whole chain resonance and those which were not [5]. The resistivity of the ribbons should be of interest, since the resistivity of a compressed pellet is known to be considerably greater than the intrinsic resistivity of the material [8].

The thermal degradation of I in air and in N_2 was studied by thermogravimetry. The temperature was raised at rates of 5—10° C per minute. Both decomposition curves were quite similar. The integral procedure decomposition temperature (IPDT), that is the temperature for 1% weight loss, was found to be 94° C in air and 100° C in N_2. The weight decreased steadily to reach in air a plateau of 29.3% residual weight at 655° C and in N_2 30% residual weight at 659° C. In air and in N_2, there was a point of inflection at ca. 200° C corresponding to about 87% residual weight. In air, the residual weight remained constant above 655° C until the end of the determination at 1327° C. In N_2, the residual weight was steady from 659 to 921° C whereupon a slow increase in weight began, rising to a peak of 32.3% residual weight at 1124° C. This was followed by a decrease in weight to 23.5% at 1327° C at which point the weight was still slowly decreasing. In air, the residue was a bright yellow friable solid, whereas in N_2 it was a black substance. The latter did not change weight on exposure to air. A recently reported investigation of organometallic polymers by coupled TG-MS showed that the metal normally remains within the residue and is not volatalized [9].

Studies of I are continuing, in particular those concerning its oxidation and cross-linking.

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