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Preliminary communication

Chromium, molybdenum, and tungsten organometallic polymeric networks with aryldiisocyanide ligands

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Abstract

Organometallic complex precursors of Cr, Mo, and W react readily with various aryldiisocyanide ligands to form insoluble polymers with the general formula $[M((CN)_2Ar)_x \cdot yH_2O]_n$, ($M = W$, $x = 3.30 \pm 0.45$; $M = Cr$, Mo, $x = 2.00 \pm 0.5$, $y \simeq 0$–3), in which the metal is in a zero-valent oxidation state. Various oxidized polymers of this type are also described.

We have been involved in the design and preparation of organometallic polymeric materials with stereochemically rigid aryldiisocyanide [1] ligands exhibiting ordered networks and having a defined microstructure. Rh^I [2–6], Ir^I [5], $Pd^{0,II}$ [7,8], and $Pt^{0,II}$ [7,8] aryldiisocyanide polymers have all been prepared by this approach. In the framework of new materials research, catalytic [7–10] and electronic [2,11,12] features of these materials have been studied. Chromium(0,II,III), molybdenum(0,II), and tungsten(0,II) homoleptic monoisocyanides of the designated oxidation states are known [13]. These metals therefore appear to be good candidates for the preparation of mixed-oxidation state polymers, and it is in this context that we report the preparation of the first Cr, Mo, and W aryldiisocyanide macromolecular networks.

$[Cr_2(OAc)_4 \cdot 2H_2O]$, $[Mo_2(OAc)_4]$, and $W_2(dmhp)_4$ (dmhp = 2,4-dimethyl-6-hydroxypyrimidine) were treated with various aryldiisocyanides. The chromium and molybdenum acetate as well as $W_2(dmhp)_4$ precursors in ethanol yielded red-brown fine powders having $\nu(CN)$ infrared absorption bands at ~ 2100, ~ 1960 (br) cm^{-1} for the Cr^0 product (**1**) and ~ 2119, ~ 1960 (br) cm^{-1}, for both the Mo^0 (**2**) and W^0 (**3**) polymers. Acetonitrile, however, is a better solvent for both the molybdenum and chromium acetate precursors and the aryldiisocyanide ligands. Brown-powdered insoluble products with similar $\nu(CN)$ infrared bands were isolated for the Mo^0 (**4**) polymers from this solvent. The reaction with the $W_2(dmhp)_4$ dimers in methylene chloride gave a dark brown-black powdered polymeric product (**5**) having $\nu(CN)$ absorptions at ~ 2119, ~ 1960 (br) cm^{-1}.

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The products show strong infrared bands at 1596 and 1576 cm^{-1} with a shoulder at 1660 cm^{-1}. These bands do not correspond to those of the precursor ligands, as would probably be the case if incomplete substitution by the aryldiisocyanides had occurred. We believe that the observed bands may be attributed to either two or four electron bridging isocyanides [8,14,15] or carbene-like metal bonds formed from isocyano functionalities with these-electron rich metals [16,17].

A ligand-to-metal ratio of three would be expected if all the aryldiisocyanides were terminally bound, as in the case of an infinite polymer. Bridging aryldiisocyanides in infinite polymers would reduce this ratio. Small oligomers would be expected to give a ligand-to-metal ratio significantly larger than that found. Thus our results appear to be consistent with the presence of extended polymeric networks. The infrared bands in the region ~ 2119 to ~ 1960 cm^{-1} are reminiscent of that of Cr, Mo, and W hexakis(monoisocyanide) complexes in which there is a significant deviation from O_h symmetry [18,19], The $\Delta\nu$(CN) found in this region for the Cr, Mo, and W polymers is however larger than that found for similar hexakis(monoisocyanide) complexes ($\Delta\nu$(CN) 40–60 cm^{-1}). These differences may arise from the symmetry changes imposed around the metal atoms due to the bridging or carbene-like aryldiisocyanide ligands mentioned above.

Microanalytical data and thermal gravimetric analysis have indicated that the materials should be formulated as $[M((CN)_2Ar)_x \cdot yH_2O]_n$ (M = W, $x = 3.30 \pm 0.45$; M = Mo, Cr, $x = 2.00 \pm 0.5$; $y \simeq 3$. The new materials immediately undergo oxidation even when only traces of oxygen are present. These oxidation changes can monitored using infrared spectroscopy; disappearance of the ~ 2100 and ~ 1960 cm^{-1} bands in the case of Cr^0 (**1**) networks is accompanied by the appearance of ν(CN) bands at ~ 2053 and ~ 2119 cm^{-1}. For the Mo^0 (**2**, **4**) and W^0 (**3**, **5**) polymers the ~ 1960 cm^{-1} band disappears. In the case of the tungsten polymers a new band at ~ 2085 cm^{-1} grows up. With the molybdenum materials a band at 2119 cm^{-1} is observed (Fig. 1).

The zero-valent polymers also underwent facile oxidations with I_2 at room temperature to give $[[M((CN)_2Ar)_xI]I \cdot yH_2O]_n$, M = W, $x = 2.9 \pm 0.32$, $y = 2.82$; M = Mo, $x = 2.2 \pm 0.33$, $y = 3.69$. Infrared data (Fig. 1) for the products of the reaction with iodine of the Mo^0 (**2**, **4**) and W^0 (**5**) polymers were similar to those of the air oxidations, but there is faster and cleaner formation of the +2 oxidation product. Reactions with $M(CNR)_6$, (M = Mo, W; R = Ph) to yield $[M(CNR)_6I]I$ complexes having the metal in a +2 oxidation state are known [20].

The UV-VIS diffuse reflectance spectra recorded for Mo^0 (**4**) and W^0 (**5**) polymers show strong very broad extended absorption bands throughout the visible range, while the W^0 (**3**), polymer reveals a distinct but broadened absorption maxima at ~ 510 nm, as do the Cr^0 (**1**) and Mo^0 (**2**) polymers. The differences between the UV-VIS absorptions and those for monomeric hexakis(arylisocyanide)-Cr^0,-Mo^0, and -W^0 complexes [21], may be due to the presence of somewhat extended *p*-π orbitals and electron delocalization between metal sites in the polymers. The Cr^0 (**1**), Mo^0 (**2**), and W^0 (**3**), aryldiisocyanide compounds reveal visible absorptions which are red shifted compared to those of the monomeric hexakis(aryliisocyanide) analogues but do not extend throughout the visible range. The broad extended absorption bands observed for Mo^0 (**4**) and Wo^0 (**5**) polymers may then be due to mixtures of these polymers with various network sizes. An additional explanation for the absorbance maxima for the polymers Mo^0 (**2**) and W^0

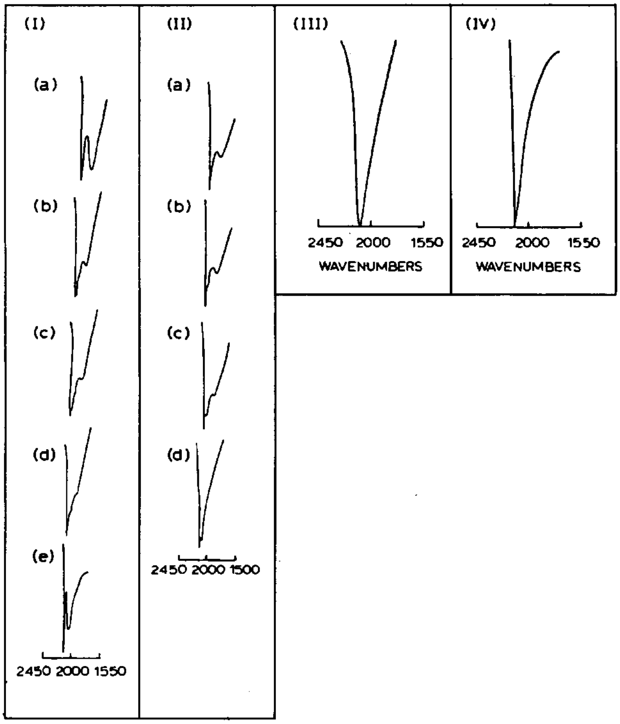

Fig. 1. Oxidations of metal aryldiisocyanide polymers, aryldiisocyanide = 4,4′ diisocyanobiphenyl. (I) M = Cr, (a) unoxidized polymer, (b) 1 day air exposure, (c) 2 days air exposure, (d) 4 days air exposure, (e) 8 days air exposure; (II) M = W, (a) unoxidized polymer, (b) 3–5 min air exposure, (c) 20 min air exposure, (d) several days air exposure. With 1 equiv. I_2 suspension in CH_2Cl_2 stirring overnight: (III) M = W, (IV) M = Mo.

(3) may be that there is some direct metal–metal interaction held together by bridging aryldiisocyanides.

The thermal decomposition of these aryldiisocyanide polymers occurs in two stages. For the W^0 (5) 4,4′-diisocyanobiphenyl polymers there is a weight loss of ~ 6% in the range 50–150 °C, corresponding to water release (~ 2.8 molecules per tungsten). An initial decomposition at ~ 250 °C corresponds to ~ 14% (by weight). A second decomposition occurs at ~ 600 °C corresponding to ~ 63% (by weight of the same polymer). We have noted that the sum of these weight losses corresponds to the expected weight percentage of the organic ligands in these coordination polymers.

Since no single crystals were available, powder X-ray diffraction was used to investigate structural parameters of these polymers. Only one strong sharp reflection was obtained, corresponding to a distance of ~ 10.75 Å for the W^0 (5) polymers. In the hopes of obtaining more ordered materials, we prepared polymers by slow precipitation in highly dilute solutions using longer reaction times. However, their powder X-ray diffraction patterns suggest that the polymers are rather disordered making structure determination by this technique impractible.

An alternative approach to the preparation of mixed oxidation polymers via copolymerization of two soluble precursor complexes having the metal in two different oxidation states, has also been investigated by use of $Mo_2(OAc)_4$ and $[Mo(CO)_4Cl_2]_2$ starting complexes and 4,4′-diisocyanobiphenyl ligands. Infrared and XPS data of the products indicate the formation of a rust-brown mixed oxidation state polymer (**6**) containing both Mo^0 and Mo^{+2} metal atoms.

Electrical conductivities measured (ac, 1 kHz) on pressed powder pellets (10 ton/cm^2) of the unoxidized W^0 (**5**) polymers are of the order of 10^{-9} ohm^{-1} cm^{-1}. None of the previously prepared mixed oxidation polymers containing W or Mo of the type described gave materials with appreciably improved electrical conductivities. We believe the very disordered nature of the polymers may very well be a major factor preventing the attainment of enhanced electrical conductivities for these materials and so our efforts are being concentrated on using the copolymerization technique of soluble metal complex precursors in two different oxidation states with more ordered polymeric systems in the hopes of obtaining new materials with optimum electronic properties.

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