Journal of Organometallic Chemistry, 350 (1988) 57–75
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Zero-valent, oxidized, and mixed oxidation state chromium, molybdenum, and tungsten aryldiisocyanide polymers

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(Received December 9th, 1987)

Abstract

New organometallic aryldiisocyanide polymers of the group 6 transition metals have been synthesized and characterized. The aryldiisocyanide chromium(0), molybdenum(0) and tungsten(0) polymers were found to be extremely sensitive towards air oxidation. Oxidized 4,4′-diisocyanobiphenyl-tungsten(II) and -molybdenum(II) polymers were prepared by the addition of iodine to the solid state zerovalent matrices. Partial oxidation of 4,4′-diisocyanobiphenyltungsten(0) polymers with iodine gave mixed valent $W^{0,II}$ polymers having W^0 and W^{II} in various ratios. Another route to mixed valent polymers involved the reaction with aryldiisocyanides of two soluble metal precursors having different oxidation states, and this approach gave mixed valent $Mo^{0,II}$ polymer with 4,4′-diisocyanobiphenyl ligands. The specific electrical conductivity of all the unoxidized, oxidized, or partially oxidized polymers was of the order of 10^{-9} Ω^{-1} cm^{-1} regardless of the preparative route used.

Introduction

A novel approach to the preparation of ordered organometallic coordination polymers having defined microstructures has been developed and reported by our group [1,2]. This approach entails the design and preparation of organometallic polymers from simple metal complex precursors, and organic polymerizing ligands. One-, two-, or three-dimensional propagation of specific coordination geometries via the organic polymerizing ligands can yield ordered porous organic networks incorporating isolated metal atoms. A series of aryldiisocyanide [3] compounds has been used effectively by our group as bridging ligands in the design and preparation of various organometallic coordination polymers [1,2,4,5,6]. Isocyanide ligands,

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0022-328X/88/$03.50

CNR (where R = alkyl, aryl), have an extensive coordination chemistry [7] that allows formation of a great many complexes with various metals. This extensive coordination chemistry makes possible the preparation of a varied multitude of organometallic coordination polymers.

In the framework of the design and preparation of new materials with possible electronic properties, we sought to investigate mixed oxidation state organometallic polymers of the type described above. In general, these mixed oxidation state polymers can be prepared by two alternative approaches, in the solid state and in solution. These approaches would be expected to yield polymers with different distributions of metals between various valence states and these distributions might influence the overall electronic properties of the materials. For this approach, metal complexes forming metal isocyanides having the metal in several low lying accessible oxidation states should be suitable starting materials. Group 6 metals readily form isocyanide complexes and furthermore are of relatively low cost. The solution chemistry of the metal monomeric isocyanide complexes $[M(CNR)_n]^{m+}$ (where M = Cr, Mo, W and R = alkyl, aryl, $m = 0$, 2, etc. $n = 5$, 6, 7) has been extensively studied and reviewed in the literature [8,9]. Monomeric isocyanide complexes of Cr, Mo, W have been prepared and studied by various investigators [9]. Hexakis(phenylisocyanide) complexes of Cr, Mo, W have been prepared, and a single crystal X-ray study on the $Cr(CNPh)_6$ showed some distortion from octahedral symmetry [11]. These latter monomeric isocyanide complexes may perhaps be viewed as monomeric analogues of potential three dimensional polymers. Unlike the rhodium aryldiisocyanide polymers, in which direct Rh–Rh interlayer distances were observed [1,2,4], all the metal atoms in these group 6 zerovalent polymers are expected to be connected only via organic bridging ligands. We hoped that the octahedral geometry expected for these zerovalent metal atoms would be less distorted in the three dimensional polymer, enabling maximum metal–ligand orbital overlap. In this case, owing to the nature of the ligands, there might be a high degree of delocalization of electrons throughout the entire matrix. A preliminary report on this work has appeared [10].

Results and discussion

Zerovalent oxidation state polymers

Tungsten

Various metal precursors for zerovalent $W(CNR)_6$ have been used previously [12–15]. The complex $W_2(dmhp)_4$ [13] (dmhp = 2,4-dimethyl-6-hydroxypyrimidine) was chosen for the preparation of tungsten(0) aryldiisocyanide polymers. The presence of the metal–metal quadruple bond is an important feature [16]. Cleavage of the metal–metal multiple bond of dimers containing a M_2L_8 skeleton (where $M = Cr_2^{4+}$, Mo_2^{4+}, W_2^{4+}, etc. and L is a labile ligand, e.g. acetate or dmhp) by π-acceptor ligands, e.g. CO, NO, and especially isocyanides CNR (R = aryl,alkyl) provides an excellent synthetic route to monomeric complexes, many of which cannot yet be readily made by other methods. $W_2(dmhp)_4$ is soluble in a wide variety of solvents and its reactions with isocyanides to give $W(CNR)_6$ have been reported [14].

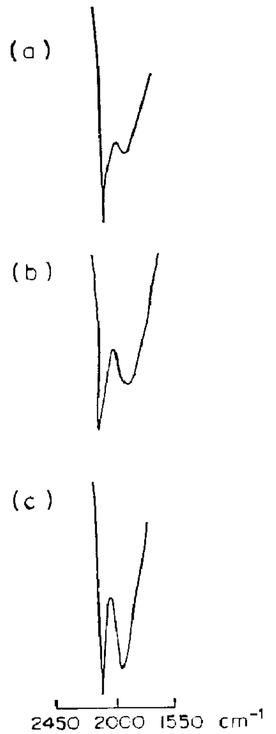

Fig. 1. ν(CN) infrared bands of terminally bridged diisocyanides: (a) W^0; (b) Mo^0; (c) Cr^0 (aryldiisocyanide = 4,4′-diisocyanobiphenyl).

The reaction of $W_2(dmhp)_4$ with aryldiisocyanides was found to be solvent dependent. In ethanol the products were red-brown fine powders, whereas in methylene chloride a dark brown-black powdered polymeric product having metallic reflectivity was obtained. Ethanol is an example of a solvent in which the initial starting materials, both the metal complexes and aryldiisocyanide ligands, are only slightly soluble. The same substances dissolve well in methylene chloride. The polymeric products isolated were insoluble, hygroscopic, and extremely sensitive to oxidation upon exposure to air. Infrared absorptions characteristic of terminally-bridged diisocyanides of the tungsten(0) aryldiisocyanide polymer were observed at ν(CN) 2119 (s), 1960 (br) cm^{-1}. These infrared absorptions are depicted in Fig. 1. In addition, medium to strong absorptions at 1576, 1596 and a shoulder at 1660 cm^{-1} were observed. The uncoordinated 4,4′-diisocyanobiphenyl ligand has a ν(CN) absorption at 2129 cm^{-1}. The lowering of the ν(CN) frequency upon coordination can be attributed to $p\pi$–$d\pi$ back-bonding. If there were ideal octahedral symmetry one ν(CN) absorption peak would be expected, and the presence of two peaks in the 1900–2200 cm^{-1} region, characteristic of terminal isocyanides, indicates deviation from such symmetry. Similar observations have been reported for the $W(CNPh)_6$ monomer [11]. This distortion from octahedral symmetry in the $M(CNAr)_6$ complexes (M = Cr, Mo, W; Ar = aryl) was much smaller when sterically hindered Ar groups, such as 2,6 diisopropylphenyl were used [11]. Deviations from octahedral symmetry were also reported for polymer-encapsulated $M(CNR)_6$, M = Cr, Mo, W, in isocyano-functionalized polysiloxane fluid matrices [17]. However, no absorption bands were found at 1576, 1596, 1660 cm^{-1} for the $M(CNPh)_6$

(M = Cr, Mo, W) monomers. The bands at 1576, 1596 and 1660 cm^{-1} are not related to the precursor dmhp ligand, which might be present if incomplete substitution of $W_2(dmhp)_4$ by aryldiisocyanides had taken place. The bands may be attributed to one or both of the following: (a) bridging aryldiisocyanides: similar bands in this range were observed for palladium(0) and platinum(0) aryldiisocyanides polymers [5]; (b) carbene-like metal bonds formed from isocyano functionalities. Owing to electron release from the electron rich tungsten(0) metal to the ligand, there is more π-character in the M–C bond and this results in bending of the MCNR system at the nitrogen atom. Several carbene-like complexes of this type have been isolated previously [18]. The value of $\Delta\nu(CN)$, the peak separation for the bands from terminal $\nu(CN)$ is larger for the polymers ($\Delta\nu(CN) \sim 150$ cm^{-1}) than for similar monomeric hexaisocyanide complexes ($\Delta\nu(CN)$ 40–60 cm^{-1}). This can be attributed to symmetry changes around the metal caused by the two effects considered above.

The tungsten(0) aryldiisocyanide polymers are oxidized immediately when exposed to air. The progress of the oxidation can be monitored by infrared spectroscopy. Upon oxidation, a new infrared band grows up at 2085–2095 cm^{-1} while the initial terminal $\nu(CN)$ bands became smaller and ultimately disappear.

Microanalyses were carried out on the polymers by initially heating them in an inert atmosphere up to temperatures of ~ 1000 °C and then continuing the pyrolysis under oxygen; this gave a narrow range of C, H, and N values, which were averaged over several microanalyses from different batches. It should be noted that the microanalyses on these polymers presented problems. Usually low carbon values were obtained, and we think that under the conditions used thermally stable tungsten carbides may be formed. Thermal gravimetric analyses (TGA) were also carried out. An additional problem was the determination of metal content. Atomic absorption techniques were initially used for determination of the metal content, but the insolubility of all polymers, made this extremely difficult, and so the results were not used in determining ligand/metal ratios; instead the metal contents were deduced from a combination of elemental analyses and TGA measurements. Elemental analyses indicate that the tungsten(0) aryldiisocyanide polymer must be formulated as $[W[(CN)_2Ar]_x \cdot yH_2O]_n$ with $x = 3.15 \pm 0.05$, $y = 2.52$ for Ar = phenyl, $x = 3.45 \pm 0.40$, $y = 2.80$ for Ar = biphenyl. Although anhydrous polymers could be prepared by heating (~ 70 °C) under vacuum (~ 0.1 torr), accurate elemental analyses could not be obtained for the anhydrous polymers owing to their hygroscopic nature.

A ligand to metal ratio of very close to three would be expected in an extremely large matrix (providing that all aryldiisocyanides were terminally bound to metals at the two isocyano functionalities), whereas a monomeric species should give a ratio of six. In oligomers of varying sizes the ratio is expected to decrease from six in relation to the oligomer size. It thus appears that the materials we have prepared are high molecular weight polymers.

Thermal gravimetric analyses carried out on the 4,4′-diisocyanobiphenyl tungsten(0) polymers showed that in an inert atmosphere there was not always total pyrolysis of the organic moieties to yield metallic tungsten. However, in an oxygen atmosphere the polymers can be totally pyrolyzed, probably owing to inhibition of metal carbide formation; metal oxide residues are probably left. That pyrolysis of 4,4′-diisocyanobiphenyl tungsten(0) polymers in an inert atmosphere was incomplete was confirmed when the TGA residue of a sample that had been heated under nitrogen up to 990 ° C was subjected to further heating but in an oxygen atmosphere. The residue lost 50% of its remaining weight at 400 ° C. This additional loss of weight was in agreement with the difference between the expected weight loss and the observed weight loss under nitrogen. Incomplete pyrolyses in an inert atmosphere may account for the low carbon values found in virtually all the microanalyses. The TGA profile of these polymers in an inert atmosphere shows that from 50 to 150 ° C the associated water molecules are eliminated. Thermal decomposition occurs in two stages: the initial stage, decomposition at ~ 250 ° C, corresponds to ~ 14% loss of weight, and the second decomposition takes place at ~ 600 ° C and corresponds to ~ 63% loss of weight. The 1,4-diisocyanobenzene tungsten(0) polymers show a similar TGA profile; i.e. water is released at 50–150 ° C, then the initial decomposition takes place at ~ 250 ° C and involves a ~ 15% loss of weight, and the second decomposition occurs at ~ 600 ° C and involves a weight loss of ~ 56%. For both these polymers, the sum of total weight loss of the two stages is in agreement with the loss of weight expected due to pyrolysis of organic ligands in the polymer having the formulation $[(W(CN)_2Ar)_x \cdot yH_2O]_n$, Ar = phenyl, $x = 3.50 \pm 0.47$, $y = 2.52$; Ar = biphenyl, $x = 3.00 \pm 0.43$, $y = 2.80$. This formulation is within the range of error of that established by elemental analyses. The significant differences in the decomposition temperatures may be due to an initial decomposition of dangling terminally coordinated ligands on the periphery of the matrix, as opposed to internal ligands in the bulk linked to metal centers by both functionalities.

Because of the insoluble nature of the organometallic aryldiisocyanide polymers, ultraviolet-visible (UV-VIS) spectra could not be recorded for solutions, and so solid-state UV-VIS diffuse reflectance spectroscopy was used. The UV-VIS diffuse reflectance spectra for the polymers prepared in different solvents were significantly different. Tungsten(0) polymers made in methylene chloride show a very strong broad absorption maximum extending throughout the visible range (see Fig. 2). Similar strong visible absorptions have been observed for a series of three dimensional $[Rh((CN)_2Ar)_2{}^+Cl^- \cdot yH_2O]_n$, $y = 0$–3 polymers in which there are direct Rh(I)- - -Rh(I) interplanar interactions [1,2]. The tungsten aryldiisocyanide polymers made in ethanol give a distinct but slightly broadened absorption maxima at ~ 510 nm. Monomeric $W(CNPh)_6$ gives a sharp absorption maximum which is blue-shifted (470 nm) compared with those observed for the polymers. The differences between the spectra of the soluble monomeric hexaisocyanides and the insoluble polymers may be due to the presence of somewhat extended π-orbitals and electron delocalization in the polymeric materials. The visible absorptions of the tungsten polymers made in ethanol are red-shifted relative to the monomeric hexakis(arylisocyanides) but do not extend throughout the visible range as do the polymers made in methylene chloride. In connection with the observed red-shifts, it is relevant to note that recent theoretical and experimental work on conjugated organic polymers (i.e. polyacetylene, polyphenylene, etc.) having extended π-systems has revealed a correlation between chain length and band gap energies, with the latter measured on the basis of absorption peaks [19]. This work indicates that as the chain length grows there is a decrease in the band gap energies, indicated by the red-shifts of the absorption maxima. The absence of extended absorptions in the higher visible and near-infrared range noted for the polymers made in ethanol may

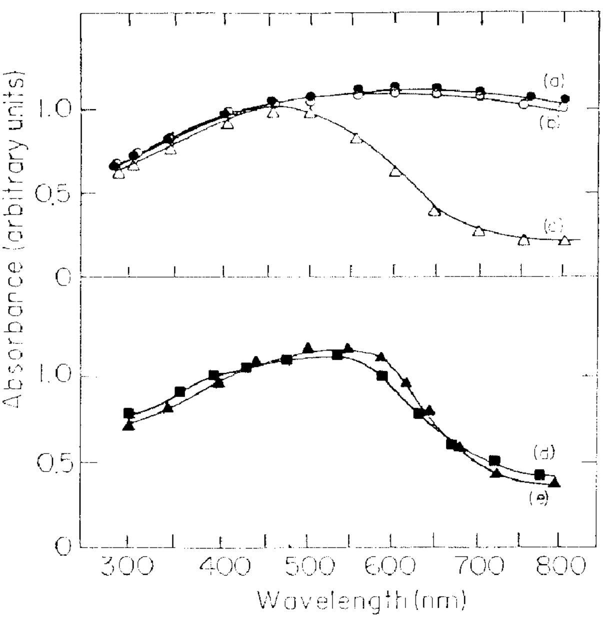

Fig. 2. Diffuse reflectance spectra for metal aryldiisocyanide polymers (compared to total reflectance and/or zero absorbance of $MgCO_3$ standard, given in absorbance): (A) a = W^0 with 1,4-diisocyanobenzene in CH_2Cl_2, b = W^0 with 4,4′-diisocyanobiphenyl in CH_2Cl_2, c = W^0 with 4,4′-diisocyanobiphenyl in ETOH; (B) d = Mo^0, as c; e = Cr^0, as c.

indicate less extended polymeric networks. This is consistent with the low solubility of the starting materials in ethanol, which results in slower reaction rates and earlier separation of polymeric matrices. Alternatively, the visible absorption maximum centering at ~ 510 nm of these systems might be due to the presence of metal–metal bonds. We observed a similar strong visible absorption in the same range for the $W_2(dmhp)_4$ precursor complex in which there are metal–metal bonds. Such metal–metal bonds could possibly remain intact in the polymer if bridging aryldiisocyanide ligands held the tungsten atoms together up to the point of complete substitution and rupture of these bonds. Rapid precipitation of these materials due to poor solubility may favour such an explanation. The broad visible absorptions in polymers made in methylene chloride may also be due to the presence of various network sizes which give rise to different maxima that cannot be resolved by the diffuse reflectance techniques we used.

Since no single crystals were available, powder X-ray diffraction was used to investigate the structural parameters of these polymers. Powder X-ray diffraction patterns obtained with the materials can be interpreted as reflections coming from metal-containing sets of planes. Only one strong sharp reflection was obtained, corresponding to a distance of 10.75 Å, for the 4,4′-diisocyanobiphenyl tungsten polymers made in methylene chloride. With the aim of obtaining more ordered materials, we prepared polymers by slow precipitation in highly dilute solutions over longer reaction times. Polymers prepared in this way, again showed one strong reflection, but this time corresponding to a 14.05 Å distance. These different distances may indicate changes in the metal–isocyanide bond. Powder X-ray diffraction patterns suggest that both polymers are disordered, and thus structural modelling using this technique is not possible.

Molybdenum and chromium

Various metal derivatives have been used for zerovalent $Mo(CNR)_6$ and $Cr(CNR)_6$ [12,15,20], and of these the dimers $Mo_2(CH_3COO)_4$ and $Cr_2(CH_3COO)_4 \cdot 2H_2O$ have been the most widely used. Reactions of these with 4,4′-diisocyanobiphenyl in ethanol gave fine red-brown to light brown powders; in these reactions the precursors were found to be less soluble, as observed for $W_2(dmhp)_4$ in ethanol. In the case of the molybdenum polymers, infrared, and UV-VIS diffuse reflectance spectra were obtained and were noted to be very similar to the tungsten polymers prepared in ethanol. The same zerovalent molybdenum precursors were more soluble in acetonitrile and the products were dark brown polymers. These latter polymers showed spectral features more similar to those of the tungsten(0) aryldiisocyanide polymers made in methylene chloride than to those of polymers made in ethanol.

The 4,4′-diisocyanobiphenyl chromium(0) polymers show ν(CN) infrared absorption bands at 2100 (vs), 1960 (br) cm^{-1}, and the Mo^0 polymers show ν(CN) infrared absorption bands at 2119 (vs), 1960 (br) cm^{-1} (Fig. 1). For the Cr^0 and Mo^0 polymers absorption bands at 1596 (med), 1660 (sh) cm^{-1} are observed as in the W^0 polymers. A ligand to metal ratio of ~ 2 was found for the 4,4′-diisocyanobiphenyl molybdenum polymers (see Experimental). As was previously mentioned, the tungsten aryldiisocyanide polymers had a ligand to metal ratio of slightly higher than 3. These different results probably could be the consequence of several factors such as different reactivity and/or solubility of the starting metal complexes, and different chemistry associated with the metal itself. It is not completely clear to us what is the relative influence of these factors. The chromium metal precursor $Cr_2(CH_3COO)_4$ is extremely sensitive towards oxidation, and consequently the isolation of chromium(0) aryldiisocyanide polymers gave problems. In addition this precursor did not have higher solubility in acetonitrile. To our knowledge no tungsten analogue of $Cr_2(CH_3COO)_4$ and $Mo_2(CH_3COO)_4$ has been reported in the literature, and so the possibility of making a W, Mo, Cr series of zerovalent group 6 metal polymers from such acetate dimers could not be tested. However, attempted preparation of zerovalent W, Mo, Cr polymers from $M_2(dmhp)_4$ type precursors was unsuccessful. When the reaction of $Cr_2(dmhp)_4$, and $Mo_2(dmhp)_4$ with aryldiisocyanides were attempted, no reaction took place in the case of the $Cr_2(dmhp)_4$, and $Mo_2(dmhp)_4$ showed a very limited reactivity. The lower reactivity of the molybdenum and chromium dimers may be a consequence of the higher stability of the metal–metal bonds in these compounds.

Oxidized polymers

Tungsten

Oxidation of W^0 polymers took place upon minimal air exposure, and over a period of days to weeks the polymers were highly oxidized. This oxidation can be monitored by infrared spectroscopy by use of the change in ν(CN) frequency of the terminally coordinated isocyanides. Air oxidation of W^0 polymers results in growth of a new infrared ν(CN) absorption band at 2085–2095 cm^{-1} and progressive disappearance of the ν(CN) bands at 2119, 1960 cm^{-1}. After complete oxidation only one sharp strong peak at 2085–2095 cm^{-1} can be seen. The change observed in

Table 1

XPS data for the 4,4′-diisocyanobiphenyl tungsten(0) polymer the iodine-oxidized 4,4′-diisocyanobiphenyl tungsten(0,II), polymer, and the iodine-oxidized 4,4′-diisocyanobiphenyl tungsten(II) polymer

Polymer	Binding energy (eV) (Found)
W^0	36.0, 34.4
$W^{0,II}$ mixed oxidation state, 50% oxidized	37.8, 35.1, 33.0
W^{II}	37.9, 35.7, 32.6

Table 2

XPS data for oxidized and partially oxidized Mo polymers

Polymer	Binding energy (eV)		
Mo^{II}	232.1	229.0	
$Mo^{II,0}$			
Chemically mixed	235.0	232.2	229.5

the infrared ν(CN) absorption bands is probably indicative of a more closely octahedral symmetry after oxidation.

Chemical oxidation of monomeric hexaisocyanides by iodine complexes has been reported [14], and we thought this might be a good way to bring about controlled oxidation of the insoluble tungsten(0) aryldiisocyanide polymers, and iodine-oxidation of the W^0 polymer was monitored by infrared spectroscpy. The results along with other pertinent results and the X-ray photoelectron spectroscopy (XPS) spectra of iodine-oxidized tungsten polymers (~ 7, ~ 51 and ~ 100%) are depicted in Tables 1 and 3 and Fig. 3 and 4. The total oxidation of W^0 polymers with iodine gave dark brown powders which can be formulated as $[[[W(CN)_2Ar]_xI]I] \cdot yH_2O]_n$ Ar = biphenyl, $x = 2.90 \pm 0.32$, $y = 2.82$. Microanalyses support this formulation. These iodine oxidized polymers gave an infrared spectrum having one strong sharp ν(CN) peak at 2085 cm^{-1} (Fig. 3). An additional feature, noted during oxidation by

Table 3

Iodinations with aryldiisocyanide polymers

Sample	No of mmol of I_2 added per W atom	No. of mmole of I_2 found per W atom (elemental analysis)	% of metals oxidized	Infrared ν(CN) (cm^{-1})
1	0.013	less than 0.018	~ 1	2119 (vs) 1960 (br) 2085
2	0.131	0.075	~ 7	2119 (vs) 1960 (br) 2085 (s)
3	0.562	0.510	~ 51	2119 (s) 2085 (s)
4	0.937	0.900	~ 90	2119 (sh) 2091 (vs)

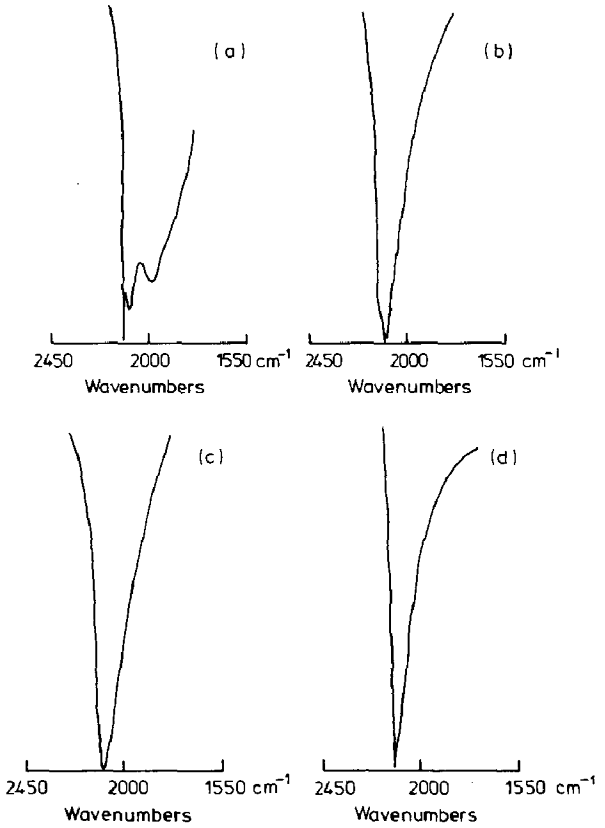

Fig. 3. ν(CN) infrared bands of terminally bridged aryldiisocyanides: (a) 4,4′-diisocyanobiphenyl tungsten polymer ~ 7% oxidized by iodine; (b) 4,4′-diisocyanobiphenyl tungsten polymer ~ 51% oxidized by iodine; (c) 4,4′-diisocyanobiphenyl tungsten polymer ~ 100% oxidized by iodine; (d) 4,4′-diisocyanobiphenyl molybdenum polymer ~ 100% oxidized by iodine.

air or iodine, is the simultaneous decrease of the absorption bands at 1596, 1576 cm^{-1}. This could be due to the rupture of bridged diisocyanides or to changes induced due to the conversion of carbene-like metal bonds into simple metal–isocyanide bonds.

Molybdenum

Molybdenum(0) polymers were also oxidized in air. The ν(CN) peak profile upon air oxidation was nearly identical to that of the tungsten polymers. However, the position of the band of the fully oxidized Mo polymers appeared at higher frequency (2119 cm^{-1}). Polymers obtained by iodine oxidation also gave a single strong ν(CN) band at 2119 cm^{-1} (Fig. 3). The elemental analyses and TGA of the Mo^{II} polymer prepared from $Mo_2(CH_3COO)_4$ and oxidized by iodine, indicate the formulation $[[([Mo(CN)_2Ar]_xI)I] \cdot yH_2O]_n$ Ar = biphenyl, $x = 2.20 \pm 0.33$, $y = 3.69$. In contrast to the tungsten case, where the non-availability of soluble tungsten precursor complexes precludes preparation of discrete W^{II} polymers, by using this method, a soluble Mo^{II} precursor complex is available. Both molybdenum hexa- and hepta-isocyanide monomeric complexes have been reported to be obtained from the $[Mo(CO)_4Cl_2]_2$ precursor [8]. Use of this precursor, the dimer, $[Mo(CO)_4Cl_2]_2$ [21],

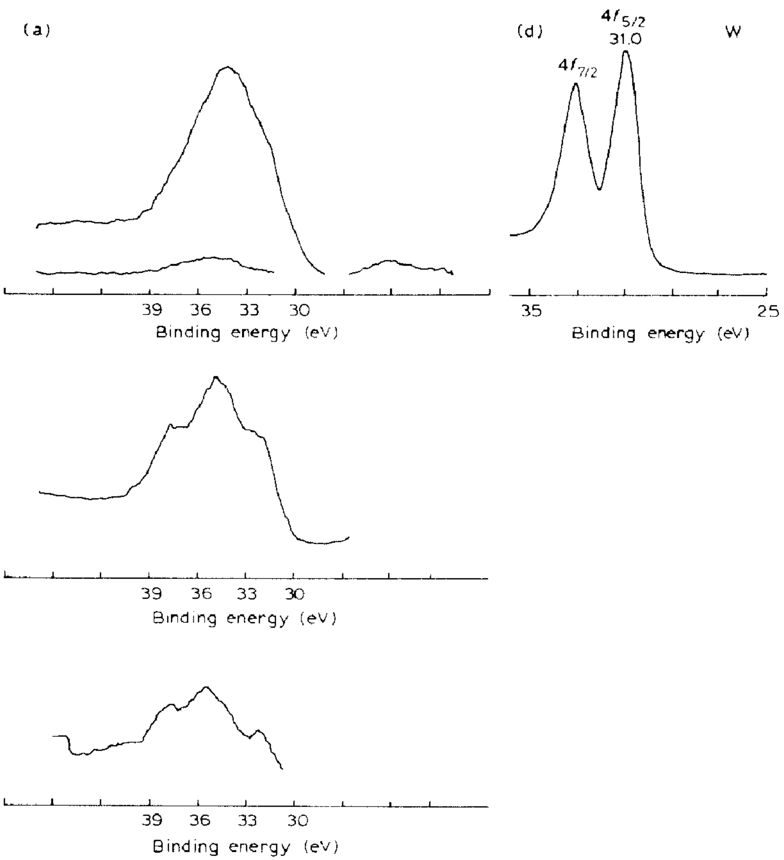

Fig. 4. (a) XPS of 4,4′-diisocyanobiphenyl tungsten polymer, unoxidized (see XPS discussion); (b) XPS of 4,4′-diisocyanobiphenyl tungsten polymer, ~ 51% iodine oxidized; (c) 4,4′-diisocyanobiphenyl tungsten polymer, almost complete iodine oxidized; (d) XPS of metallic tungsten.

gave Mo^{II} oxidized polymers without the need to use external chemical oxidants with the solid state Mo^0 polymers. With these polymers the metal is fully oxidized from the outset and so we can be sure that all metal atoms are in the M^{II} oxidation state, whereas with air or chemical oxidants the reactions are diffusion-dependent and complete oxidation is never certain. The reaction of $[Mo(CO)_4Cl_2]_2$ with 4,4′-diisocyanobiphenyl gave a yellow powder in a very fast reaction; the reactivity was reminiscent of that with other metal carbonyl chloride dimers, for example of rhodium aryldiisocyanide polymers [2]. Elemental analyses and TGA of the Mo^{II} polymer prepared from $[Mo(CO)_4Cl_2]_2$ indicate the formulation $[[(Mo[(CN)_2Ar]_x Cl)Cl] \cdot yH_2O]_n$ Ar = biphenyl, $x = 2.40 \pm 0.13$, $y = 3.65$. The infrared spectra show the same $\nu(CN)$ band as in the molybdenum polymers oxidized by iodine or by air exposure, indicating the oxidation state Mo^{II}. Although the same $\nu(CN)$ band of the terminal isocyanide is observed for this Mo^{II} polymer (prepared from $[Mo(CO)_4Cl_2]_2$), the infrared absorption bands at 1576, 1596 cm^{-1} present as in the Mo^0 case are absent. This favours the hypothesis of the presence of carbene-like bonds and/or bridging isocyanides in the M^0 (M = Cr, Mo, W) polymers. The less electron rich M^{II} (relative to M^0) systems will release less electron density from the metal to the ligands, and so the metal isocyanide bonds will have less π-character, and the M–CNR form will be more dominant. In this situation the carbene-like metal–isocyanide bond is not expected to be formed. It could also be expected that in this electron deficient metal system there will be a lower tendency to form bridged isocyanides and it will be more likely that simple metal–isocyanide terminal bonds will be formed. This is consistent with the fact that the absorption bands at 1576, 1596 cm^{-1} decrease upon oxidation with iodine.

Chromium

We found that the Cr polymers were less stable toward oxidation. High concentrations of iodine or long exposure to air appeared to cause partial decomposition of the matrices. With monomeric chromium isocyanide complexes the possibility of obtaining Cr^{III} by oxidation of $Cr(CNR)_6$ monomers with $SbCl_5$ and $NOBF_4$ has been examined [9]. Attempts to obtain analogous organometallic polymers having Cr^{III} atoms using the above oxidants with chromium(0) aryldiisocyanide polymers did not succeed. Even under very mild conditions, i.e., low temperatures (−30 °C) and low oxidant concentration, either decomposition of the polymeric matrix and/or reaction at the isocyanide functionality occurred as revealed by the presence of a much less intense ν(CN) band after oxidation. The oxidation of 4,4′-diisocyanobiphenyl chromium(0) polymers by air was monitored by infrared spectroscopy. As previously noted, the unoxidized polymers show two absorptions corresponding to coordinated terminally bridged diisocyanide at ν(CN) 2100 (vs), 1960 (br) cm^{-1}. After several hours of exposure to the air, two new bands grow up, at 2120, 2060 cm^{-1}, and at the same time the 2100, 1960 cm^{-1} peaks decrease. After a few days, only the 2120, 2060 cm^{-1} bands remain. After several further days these bands have much lower intensities. Oxidation by I_2 always caused a decrease in the terminal isocyanide bands, as did oxidation by $SbCl_5$ or $NOBF_4$. In some cases very weak absorptions were observed at 2270 and 2200 cm^{-1} and less weak (but diminished in relation to the parent peaks) at 2120, 2060 cm^{-1}. In no cases were bands corresponding to only one valence state observed. From these results the following assignments are appropriate: Cr^0 polymer ν(CN) 2100, 1960 cm^{-1}; Cr^I polymer ν(CN) 2120, 2060 cm^{-1}; Cr^{II} polymer ν(CN) 2200 cm^{-1}; Cr^{III} polymer ν(CN) 2270 cm^{-1}. Owing to the synthetic difficulties we decided not to investigate further the possibility of preparing mixed oxidation state chromium aryldiisocyanides. This type of investigation was continued with the W and Mo polymers.

Mixed oxidation state

Various organometallic polymers with mixed oxidation states have been reported. These materials have demonstrated significant electrical conductivity [22,23]. We felt that our approach towards the design of organometallic polymers would lead to more versatile preparations of mixed oxidation state materials in which it might be possible to alter the relative positions of the metal atoms in the two different oxidation states, possibly resulting in a change in conducting properties. As previously mentioned, with our systems mixed oxidation state polymers may be made either by reactions of the solid state polymeric matrix having metals in one discrete oxidation state or by choosing two soluble precursor complexes having the metal in two different oxidation states and then polymerizing them simultaneously with aryldiisocyanides.

Solid state precursor

In the first method a chemical oxidant, such as an iodine in solution, is allowed to partially oxidize the metal atoms of the aryldiisocyanide polymer. Presumably, since the iodine has to diffuse into the pores of the polymer to oxidize the internal metal atoms, the external metal atoms will be preferentially oxidized. In contrast, when soluble precursors having the metal in different oxidation states are used there should (on the assumption of the same reactivity for the two precursors) be a more or less random mixing of metal atoms in different oxidation states in the final polymer. In an explanation of the approach involving partial oxidation of the solid polymer iodine was used as the oxidant. The iodine was added to the tungsten aryldiisocyanide polymers in less than stoichiometric quantities, in order that only some of the metal centres will be oxidized. (Partial oxidation of metal centres in organometallic polymers using iodine has been previously reported [22,23].) This resulted in mixed oxidation state polymers having W^0 and W^{II} in different relative amounts. Polymers having roughly 1, 7, 51, 90, and up to 100% of the tungsten atoms oxidized by iodine were prepared in this way. As expected the mixed oxidation state $W^{0,II}$ polymer gives a ν(CN) band at 2085 cm^{-1} which increases in intensity as the iodine content increases and thus the content of W^{II} increases. The completely oxidized W^{II} polymers shows only this absorption band (Fig. 3). The iodine content (Table 3) increases with the amount of added iodine. The effect of the amount of iodine used on the oxidation state was also investigated by use of XPS (Fig. 4). The characteristic peaks of metallic tungsten are depicted in Fig. 4d. The XPS for the W^0 polymer is composed of one broad peak centred at 34.4 eV with a shoulder at ~ 36 eV. The broad band spreads are 5 eV, and so overlap between the expected peaks seems likely. The broadness of the peaks may be caused by charging effects. Alternatively owing to its sensitivity towards air oxidation, the W^0 polymer may be oxidized to some extent, and this may have influenced the peak shape and position. The partially oxidized $W^{0,II}$ polymer (~ 50% W atoms in oxidation state II) show three tungsten XPS peaks. Such a spectrum could be expected if there were an overlap between W^0 and W^{II} peaks. If this is the case, then the peak at higher binding energy (37.8 eV) may be assigned to the $4f_{5/2}$ peak of the W^{II}, and the peak at lower binding energy (33 eV) to the $4f_{7/2}$ peak of W^0, and the middle peak (35.1 eV) might result from overlapping of the $4f_{7/2}$ peak of W^{II} with the $4f_{5/2}$ peak of the W^0. An increase in intensity of the middle peak relative to the other two, would be expected from such an overlap. The W^{II} polymer spectrum also shows three peaks, but the lower energy band at 32.6 eV has a much lower intensity than the other two. This could be due to the presence of an unoxidized "nucleus" of W^0 atoms in the W^{II} matrix arising from poor I_2 diffusion towards the less exposed metals of the polymer. Experimental support for this suggestion comes from elemental analyses, since the amount of iodine present was always less than the theoretical amount expected on the basis of the amount added (Table 3). If a small number of W^0 atoms is present a much lower relative intensity should be expected, and this is observed for the peak at lowest binding energy (32.6 eV) which can be assigned to the W^0 $4f_{7/2}$ peak. The middle peak at 35.7 eV may involve overlap of peaks from W^{II}, predominantly, and W^0. The highest binding energy peak at 37.9 eV may then be that corresponding to the $4f_{5/2}$ peak of W^{II}. We should note that XPS is essentially a surface technique, and we could only obtain information for up to 80 Å from the surface, but we did not find any significant differences between the XPS data for 30 Å and those for 80 Å.

Discrete oxidation state solution precursors

An alternative approach investigated involved use of solutions of precursors in discrete oxidation states. In this approach soluble complex precursors with different oxidation states are treated in solution with bridging aryldiisocyanides to give mixed oxidation state matrices. The limiting factor here is to find two metal precursors with different oxidation states that are soluble in the same solvent. In the case of molybdenum, this was possible since $Mo_2(CH_3COO)_4$ and $[Mo(CO)_4Cl_2]_2$ were both soluble in acetonitrile. For purposes of comparison, simple physically mixed Mo^0 and Mo^{II} polymeric samples were made. Infrared spectra of the chemically and physically mixed oxidation state polymers showed different peak shapes, intensities, and band positions for both these samples (Fig. 5). Elemental analysis and TGA showed the formulation of the mixed oxidation state polymer ($Mo^0 + Mo^{II}$) to be $[[Mo[(CN)_2Ar]_xCl_z] \cdot yH_2O]_n$ (Ar = biphenyl, $x = 2.15 \pm 0.12$, $y = 2.39$, $z = 0.78$).

In the diffuse reflectance UV-VIS spectra only slight differences were observed for the above mixed oxidation state polymers obtained by physical and chemical means. In both cases the spectra profiles lay between the respective Mo^0 and Mo^{II} spectra. This may be because the Mo^0 aryldiisocyanide polymers have such an extended visible absorption envelope, that it could be difficult to see certain

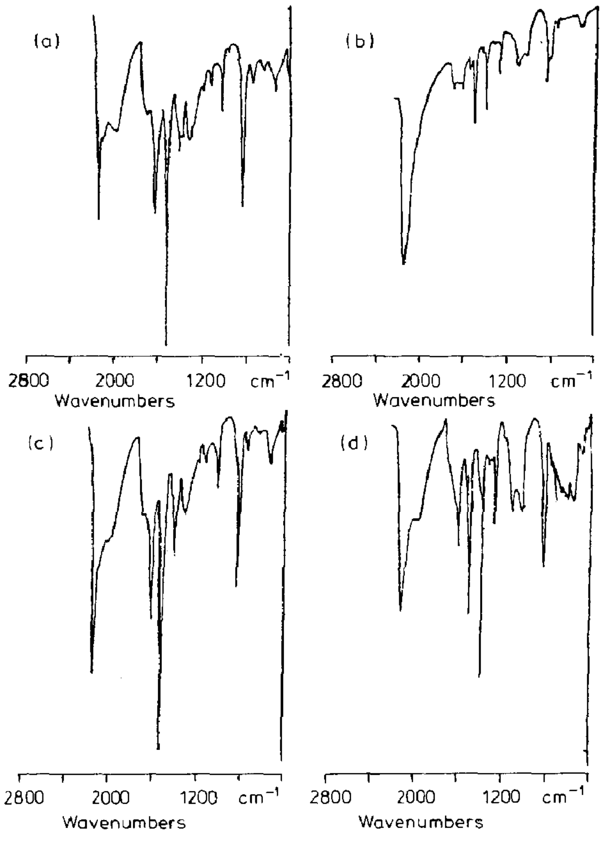

Fig. 5. Infrared spectra of 4,4′-diisocyanobiophenyl molybdenum polymers (in acetonitrile): (a) zerovalent polymer; (b) molybdenum(II) polymer made from soluble metal complex $[Mo(CO)_4Cl_2]_2$; (c) physical mixture of polymers (a) and (b); (d) chemically prepared mixed oxidation state (0,II) polymer.

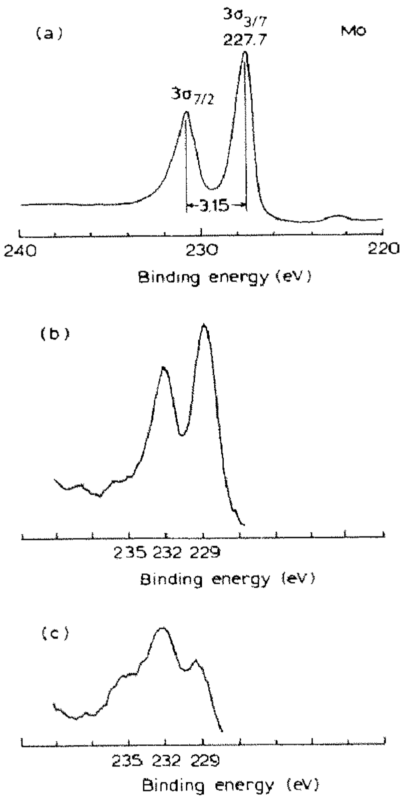

Fig. 6. XPS of (a) metallic molybdenum, (b) 4,4′-diisocyanobiphenyl molybdenum polymer prepared from $[Mo(CO)_4Cl_2]_2$; (c) chemically prepared mixed oxidation state 4,4′-diisocyanbiphenyl molybdenum polymer.

changes, and furthermore the resolution may be insufficient for observation of any changes. XPS data were obtained for the 4,4′-diisocyanobiphenyl molybdenum polymer (oxidized and mixed oxidation state) and the results are shown in Table 2; and Fig. 6b,c, for the peaks of metallic Mo see Fig. 6a. The Mo^{II} polymer gave two peaks of the expected position intensities [24]. The mixed oxidation state polymer spectrum showed three peaks. We assigned the peak at highest energy (235 eV) to the Mo^{II} $3d_{3/2}$, and so there is a shift of 3 eV to higher energies compared with the spectrum in Fig. 6b. Such shifts are known often to occur as a result of charging effects.

Conclusions

On the basis of information in the literature and on our initial assumptions concerning delocalization in these polymers, we expected to observe order of magnitude changes in conductivity upon oxidation regardless of which partial oxidation technique was used. However, for all of the polymers tested in this study, only small increases in conductivity values were observed for totally or partially oxidized polymers (see Table 4). The fact that similar conductivities are observed may indicate that in all the polymers prepared, the relative positions of the metal atoms in the different oxidation states is not a major factor in determining the

Table 4

Specific conductivities of tungsten and molybdenum aryldiisocyanide polymers

No. [a]	Metal aryldiisochanide polymers	Pellet thickness (mm)	Specific conductivity (Ω^{-1} cm^{-1} $\times 10^{-9}$)
1	W^0	1.00	0.96
2	**1** oxidized in air 1 h	1.20	0.80
3	**1** oxidized in air	1.20	1.03
4	**1** oxidized in air 24 h	1.00	1.09
5	**1** oxidized in air 48 h	0.80	1.04
6	**1** oxidized in air 64 h	0.75	0.95
7	**1** oxidized by I_2 ~1%	0.75	0.12
8	**1** oxidized by I_2 ~ 7%	0.80	0.14
9	**1** oxidized by I_2 ~ 51%	0.80	0.38
10	**1** oxidized by I_2 ~ 90%	0.70	0.33
11	**1** oxidized by I_2 ~100%	1.00	1.40
12	**1** + **11** + W_2(dmhp)$_4$	0.60	0.52
13	**12** oxidized in air	0.60	0.61
14	Mo^0	0.60	0.11
15	**14** oxidized by I_2 ~100%	0.60	0.91
16	$Mo^0 + Mo^{II}$ chem. mixed	0.55	0.25
17	$Mo^0 + Mo^{II}$ phys. mixed	0.60	0.24

[a] **1**: Tungsten(0) aryldiisocyanide polymers (with 1,4-diisocyanobenzene or 4,4′-diisocyanobiphenyl) in methylene chloride.
2–6: Polymer No. **1** with 4,4′-diisocyanobiphenyl exposed to air.
7–11: Polymer No. **1** with 4,4′-diisocyanobiphenyl oxidized by iodine.
12: Product of the reaction of **1** + **11** + W_2(dmhp)$_4$.
13: Polymer No. **12** exposed to air several days.
14: 4,4′-Diisocyanobiphenyl molybdenum(0) polymer in acetonitrile.
15: Polymer No. **14** oxidized by iodine.
16: $Mo^0 + Mo^{II}$ chemically mixed.
17: $Mo^0 + Mo^{II}$ physically mixed (as above).

enhanced conductivity. Instead a more important role probably is played by the overall order in the polymers, that is, an ideal octahedral geometry around the metal atoms in these polymers would be expected to enhance orbital overlap between metal atoms and organic ligands and thus possibly increase the conductivities. X-ray diffractometric studies indicate the parent polymers to be quite disordered, and a distorted octahedral symmetry about the metal atoms was confirmed by infrared spectroscopy. These factors partly account for our failure to observe higher conductivities or more significant conductivity changes upon partial oxidation with the different polymers. Application of our approaches to mixed oxidation state organometallic polymers with more ordered systems is being investigated.

Experimental

All reactions were carried out under argon, either in a glove box or by Schlenk techniques, and samples were kept under argon until the measurements were finished. All solvents were distilled and dried by standard procedures. They were further degassed and kept under argon. The starting materials aryldiisocyanides [3],

$W_2(dmhp)_4$ [13], $Mo_2(CH_3COO)_4$ [25], $Cr_2(CH_3COO)_4$ [25], $Mo_2(dmhp)_4$ [13], $Cr_2(dmhp)_4$ [13], $[Mo(CO)_4Cl_2]$ [21] were made by published procedures.

Spectra in the UV-VIS range were recorded on a Cary 15 spectrophotometer fitted with a diffuse reflectance attachment. Infrared spectra as KBr pellets were recorded on a Nicolet MX-1 Fourier Transform spectrophotometer. Thermal gravimetric analyses were normally carried out with a Mettler TA 3000 thermal analysis system under nitrogen (but under oxygen when appropriate) at a scan rate of 20 degrees per minute. Powder X-ray diffraction measurements were obtained by diffractometric trace techniques involving a scan speed of 1° (2θ) min^{-1}, a Debye Scherrer Camera, and a pinhole camera, all using Cu radiation. Samples were prepared in the the glove box in quartz 1 mm capillary tubes sealed with epoxy glue. X-ray photoelectron spectra (XPS) were obtained with a Kratof EF 300 instrument with alumina radiation ($h\nu$ 1468.40 eV). Measurements of the electrical conductivity (ac, 1 kHz) across compressed powder pellets (10 ton cm^{-2}) under argon were made using a specially designed holder press and a 1680 digital automatic capacitance bridge supplied by the General Radio Co. of Concod, Massachusetts, USA.

Preparation of metal(0) aryldiisocyanide polymers (M = W, Mo, Cr)

Preparation of tungsten(0) aryldiisocyanide polymers in CH_2Cl_2

The general procedure for the preparation of tungsten(0) aryldiisocyanide polymers involved dropwise addition (~ 1/2 hr) of a CH_2Cl_2 solution (15 ml) of the aryldiisocyanide ligand (2.45 mmol) to a magnetically stirred solution of $W_2(dmhp)_4$ (0.32 g, 0.37 mmol) in the same solvent (25 ml) at room temperature (~ 25 °C). A dark brown-black product separated very rapidly, the mixture was stirred overnight, and the precipitate was filtered off, washed with CH_2Cl_2 (2 × 10 ml) and dried under vacuum (0.1 torr) overnight at ambient temperature. The product was obtained as a dark powder in quantitative yields with respect to the starting $W_2(dmhp)_4$. These substances are extremely air sensitive and hygroscopic, and so must be handled in an inert atmosphere.

5[W(1,4-diisocyanobenzene)$_x$ · *y*$H_2O]_n$; $x = 3.15 \pm 0.05$, $y = 2.52$. Elemental analyses: found (calc.) (%) (calc. for $C_{24}H_{12}N_6W$; $x = 3$, $y = 0$); C, 46.68(50.72); H, 3.44(2.13); N, 13.94(14.79); (calc. for $x = 3.15$, $y = 2.52$); C, 46.68(47.81); H, 3.44(2.81); N, 13.94(13.94). Thermal gravimetric analyses (under nitrogen); ~ (50 °C to 150 °C) release of water, ~ 6.7% amount of weight loss. ~ 250 °C first decomposition, ~ 15% amount of weight loss [26*]; ~ 600 °C second decomposition, ~ 56% amount of weight loss [26]. Infrared ν(CN) (KBr): 2119 (s), 1960 (br), 1660 9w), 1596, 1576 (s) cm^{-1}.

[W(4,4′-diisocyanobiphenyl)$_x$ · yH_2O]; $x = 3.45 \pm 0.40$, $y = 2.80$. Elemental analyses: found (calc.) (%) (calc. for $C_{42}H_{34}N_6W$; $x = 3$, $y = 0$); C, 56.53(63.32); H, 4.12(3.04); N, 10.30(10.55); (calc. for $x = 3.45$, $y = 2.80$); C, 56.53(61.78); H, 4.12(3.56); N, 10.30(10.30). Thermal gravimetric analyses (under nitrogen): ~ (50 °C to 150 °C) release of water, ~ 5.96% amount of weight loss; ~ 250 °C first decomposition, ~ 14% amount of weight loss [26*]. ~ 600 °C second decomposition, ~ 63% amount of weight loss [26*]. Infrared ν(CN) (KBr): 2119 (s), 1960 (br),

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* Reference number with asterisk indicates a note in the list of references.

1660 (w); 1596, 1576 (s) cm^{-1}. X-ray diffraction lines at: 10.75 (vs), 6.7 (w) Å. XPS: (most intense W peaks) broad peak centering at 34.4 eV with shoulder at 36 eV.

Preparation of 4,4′-diisocyanobiphenyl molybdenum(0) polymers in CH_3CN

A CH_3CN solution (20 ml) of 4,4′-diisocyanobiphenyl (0.420 g, 2.06 mmol) was added dropwise (~ 1/2 h) to a magnetically stirred solution of $Mo_2(CH_3COO)_4$ (0.133 g, 0.31 mmol) in the same solvent (30 ml) at room temperature (~ 25 °C). A brown product separated slowly, and the mixture was stirred for three days. The solid was filtered off, washed with CH_2Cl_2 (2×10 ml), and dried under vacuum (0.1 torr) overnight at ambient temperature. The product was obtained as a brown powder in quantitative yield with respect to $Mo_2(CH_3COO)_4$. These polymers are extremely air sensitive and hygroscopic, and must be handled in an inert atmosphere.

$[Mo(4,4'\text{-diisocyanobiphenyl})_x \cdot yH_2O)]_n$ $x = 2.00 \pm 0.30$, $y = 1.9$. Elemental analyses: found (calc.) (%) (calc. for $C_{42}H_{24}N_6Mo$, $x = 3$, $y = 0$); C, 62.70(71.28); H, 3.93(3.42); N, 10.41(11.86); (Calc. for $x = 2.00$, $y = 1.90$); C, 62.70(66.67); H, 3.93(3.96); N, 10.41(10.41). Thermal gravimetric analyses (under nitrogen): ~ (50 to 150 °C) release of water, ~ 6.5% amount of weight loss ~ 449 °C first decomposition ~ 27% amount of weight loss [26*]. ~ 710 °C second decomposition ~ 53.5% amount of weight loss [26*]. Infrared ν(CN) (KBr): 2119 (s), 1960 (br), 1660 (sh), 1596 (S) cm^{-1}.

Preparation of 4,4′-diisocyanobiphenyl metal(II) polymers (M = W, Mo, Cr)

Preparation of $[[[W(4,4'\text{-diisocyanobiphenyl})_x I]I] \cdot yH_2O]_n$ $x = 2.90 \pm 0.32$, $y = 2.82$. The insoluble brown-black 4,4′-diisocyanobiphenyltungsten(0) polymer prepared in CH_2Cl_2 (0.2 g, 0.21 mmol) was stirred overnight at room temperature in a CH_2Cl_2 solution (20 ml) of iodine (64 mg, 0.25 mmol). The product was then filtered off, washed with CH_2Cl_2 (3×10 ml) and dried under vacuum (0.1 torr) overnight at ambient temperature. A dark violet-black powder was obtained in quantitative yield with respect to the starting polymer. Elemental analyses: found (calc.) (%) (calc. for $C_{42}H_{24}N_6W\ I_2$; $x = 3$, $y = 0$): C, 41.01(47.61); H, 2.38(2.28); N, 7.34(7.93); I, 23.16(21.02); (calc for $x = 2.9$, $y = 2.82$) C, 41.01(45.09); H, 2.38(2.69); N, 7.34(7.52); I, 23.16(23.51). Thermal gravimetric analyses: (i) under nitrogen, > (50 °C to 150 °C) release of water ~ 5.5% amount of weight loss (in nitrogen atmosphere, incomplete decomposition); (ii) under oxygen, ~ 270 °C first decomposition (under oxygen) ~ 31.3% amount of weight loss ~ 450 °C second decomposition (under oxygen) ~ 47.8% amount of weight loss. Infrared ν(CN) (KBr) 2085 (vs), 1598 (med), 1643 (w) cm^{-1}. XPS: (most intense W peaks) 37.9 (med), 35.7 (s), 32.6 (w) eV.

Preparation of $[[[Mo(4,4'\text{-diisocyanobiphenyl})_x I]I] \cdot yH_2O]_n$; $x = 2.20 \pm 0.33$, $y = 3.69$. The insoluble 4,4′-diisocyanobiphenylmolybdenum(0) polymer prepared in CH_3CN (0.2 g, 0.37 mmol) was stirred overnight at room temperature in a CH_2Cl_2 solution (20 ml) of iodine (0.126 g, 0.50 mmol). The product was then filtered off, washed with CH_2Cl_2 (3×10 ml), and dried under vacuum (0.1 torr) overnight at ambient temperature. The product was obtained as a dark brown powder in quantitative yield with respect to the starting polymer. Elemental analyses: found (calc) (%) (calc. for $C_{42}H_{24}N_6MoI_2$ $x = 3$, $y = 0$); C, 46.16(52.35); H, 2.92(2.49); N, 7.36(8.73); I, 29.64(26.38); (calc. for $x = 2.20$, $y = 3.69$); C, 46.16(42.72); H, 2.92(2.91); N, 7.36(7.12); I, 29.64(29.36). Thermal gravimetric analyses (under nitrogen): ~ (50 to 150 °C) release of water ~ 7.8% amount of weight loss (incomplete decomposition under nitrogen). Infrared ν(CN) (KBr) 2119 (vs), 1676 (sh), 1609 (med) $\mathrm{cm^{-1}}$.

Preparation of $[[[Mo(4,4'\text{-}diisocyanobiphenyl)_xCl]Cl]\cdot yH_2O]_n$, $x = 2.40 \pm 0.13$, $y = 3.65$. A CH_3CN solution (25 ml) of 4,4′-diisocyanobiphenyl (0.56 g, 2.75 mmol) was added dropwise (~ 1/2 h) into a magnetically stirred solution of $[Mo(CO)_4Cl_2)]_2$ (0.2 g, 0.36 mmol) in the same solvent (25 ml) at room temperature (~ 25 °C). The initially yellow solution rapidly became orange. The mixture was stirred overnight and The yellow-orange precipitate was then filtered off, washed with CH_2Cl_2 (2 × 10 ml), and dried under vacuum (0.1 torr) overnight at ambient temperature. The product was obtained in quantitative yield with respect to the starting $[Mo(CO)_4Cl_2)]_2$.

Elemental analyses: found (calc.) (%) (calc. for $C_{42}H_{24}N_6Mo\ Cl_2$, $x = 3$, $y = 0$): C, 52.07(64.70); H, 3.44(3.08); N, 9.29(10.78); Cl, 9.53(9.11); (calc. for $x = 2.40$, $y = 3.65$): C, 52.07(55.83); H, 3.44(3.70); N, 9.29(9.30); Cl, 9.53(9.83). Thermal gravimetric analyses; (i) under nitrogen: ~ (50 to 150 °C) release of water ~ 8.1% amount of weight loss; ~ 320 °C first decomposition ~ 9.5% amount of weight loss [26*]; ~ 650 °C second decomposition ~ 78.9% amount of weight loss [26*]; (ii) under oxygen ~ (50 to 150 °C) release of water, ~ 8.2% amount of weight loss; ~ 350 °C first decomposition ~ 84.8% amount of weight loss [26*]. Infrared ν(CN) (KBr): 2119 (vs) $\mathrm{cm^{-1}}$. XPS: (most intense Mo peaks) 232, 229 eV.

Preparation of mixed oxidation state group 6 metals 4,4′-diisocyanobiphenyl polymers (I_2 oxidized)

Preparation of mixed oxidation state 4,4′-diisocyanobiphenyltungsten(0,II) polymers (I_2 oxidized). The procedure was identical to that used for the preparation of W^{II} (I_2 oxidized) polymers, but less than stoichiometric amounts of I_2 were added.

Preparation of mixed oxidation state 4,4′-diisocyanobiphenylmolybdenum(0,II)polymers. A solution of 4,4′-diisocyanobiphenyl (0.45 g, 2.21 mmol) in CH_3CN (25 ml) was added dropwise (~ 1/2 h) to a magnetically stirred solution of $Mo_2(CH_3COO)_4$ (0.08 g, 0.186 mmol) and $[Mo(CO)_4Cl_2]_2$ (0.07 g, 0.126 mmol) in CH_3CN (25 ml). The yellow solution became brownish-orange. The mixture was then stirred at room temperature overnight, and the light brown precipitate was then filtered off, washed with CH_2Cl_2 (2 × 10 ml), and dried under vacuum (0.1 torr) overnight at room temperature. The product was obtained in 72% yield.

Elemental analyses: found (calc.) (%) (calc. for $C_{42}H_{24}N_6Mo/Cl$, $x = 3$, $y = 0$); C, 60.13(67.79); H, 4.13(3.23); N, 9.96(11.30); Cl, 4.58(5.01); (calc. for $x = 2.15$, $y = 2.39$, Cl, 0.78.) C, 60.13(59.68); H, 4.13(3.66); N, 9.96(9.95); Cl, 4.58(4.57). Thermal gravimetric analyses in oxygen: ~ (50 to 150 °C) release of water ~ 7.1% amount of weight loss ~ 370 °C first decomposition ~ 82.9% amount of weight loss [26*]. Infrared ν(CN) (KBr): 2119 (vs), 1980 (br), 1598 (med) $\mathrm{cm^{-1}}$. XPS: (most intense Mo peaks) 235, 232.2, 229.5 eV.

Acknowledgements

The authors gratefully acknowledge a gift of $Mo(CO)_6$ from the Climax Molybdenum Company a division of Amax. XPS measurements were made by Dr.

Stephen A. Lawrence at Brunel University, U.K. Funding was generously provided by NCRD (Israel).

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