$[Cr(CNC_6H_{11})_7](PF_6)_2$, 80083-28-9; $[Cr(CNC(CH_3)_3)_4(P(C_2H_5)_3)_2](PF_6)_2$, 80083-32-5; $[Cr(CNC(CH_3)_3)_4(P(C_3H_7)_3)_2](PF_6)_2$, 80063-24-7; $[Cr(CNC(CH_3)_3)_4(P(C_4H_9)_3)_2](PF_6)_2$, 80063-26-9; $[Cr(CNC(CH_3)_3)_4(dppe)](PF_6)_2$, 80063-28-1; $[Cr(CNC(CH_3)_3)_5(dppe)](PF_6)_2$, 80083-34-7; $[Cr(CNC_6H_{11})_4(P(C_2H_5)_3)_2](PF_6)_2$, 80063-30-5; $[Cr(CNC_6H_{11})_4(P(C_3H_7)_3)_2](PF_6)_2$, 80063-32-7; $[Cr(CNC_6H_{11})_4(P(C_4H_9)_3)_2](PF_6)_2$, 80083-36-9; $[Cr(CNC_6H_{11})_4(dppe)](PF_6)_2$, 80063-34-9; $[Cr(CNC_6H_{11})_5(dppe)](PF_6)_2$, 80106-37-2.

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Hexagonal Structural Modification of $[Rh(dicbp)_2{}^+Cl^-]_n$ and Two-Dimensional $[Ir(dic)_2{}^+Cl^-]_n$ Polymers

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The preparation and characterization of a hexagonal structural modification of $[Rh(dicbp)_2{}^+Cl^-]_n$ (dicbp = 4,4′-diisocyanobiphenyl) is described: This stacked layer polymer contains an extensive network of columnar metal chains with intrachain Rh–Rh distances of 3.54 Å. The hexagonal polymer undergoes pressure-induced isomerization to the tetragonal structural modification. The preparation and characterization of a series of iridium polymers of the type $[Ir(dic)_2{}^+Cl^-]_n$ (dic = diisocyanide) are also described. The new iridium polymer consists of two-dimensional layered structures.

Introduction

Recently, we have reported the formation and characterization of coordination polymers of the type $[Rh(bridge)_2{}^+Cl^-]_n$ with stereochemically rigid diisocyanide linkages of different bridging geometries (e.g., collinear,[1] bent,[2] and parallel[3]). These rhodium(I) polymers consist of stacked layer tetragonal structures and contain extended networks of columnar metal chains.

The current study describes the formation and characterization of a hexagonal structural modification of $[Rh(dicbp)_2{}^+Cl^-]_n$, as well as certain two-dimensional diisocyanoiridium(I) polymers.

Experimental Section

Diisocyanides,[4] $[Rh(CO)_2Cl]_2$,[5] and $[IrCl(cod)]_2$[6] (cod = 1,5-cyclooctadiene) were prepared according to published procedures. Reactions were routinely carried out under argon atmosphere. Solvents used during the course of this investigation were dried, deoxygenated, and freshly distilled before being used. Microanalyses were performed by Dornis und Kolbe Mikroanalytisches Laboratorium, Mulheim, West Germany, as well as by the Microanalytical Laboratory at the Weizmann Institute.

Infrared spectra were recorded on a Perkin-Elmer 237 grating IR spectrometer and calibrated with the aid of a polystyrene film. Diffuse-reflectance spectra were measured on a Cary-15 spectrophotometer. Powder X-ray diffractometric traces were obtained on a Phillips diffractometer using filtered Cu radiation and a scan speed of 1° (2θ) min^{-1}.

$[Rh(dicbp)_2{}^+Cl^-]_n$ (Hexagonal Modification). A solution of 4,4′-diisocyanobiphenyl (0.79 g, 3.85 mmol) in CH_2Cl_2 (50 mL) was added at a steady rate of 0.3 mL min^{-1} into a magnetically stirred solution of $[Rh(CO)_2Cl]_2$ (0.15 g, 0.39 mmol) in the same solvent (50 mL) at ambient temperature (25 °C). The bright green polycrystalline polymer $[Rh(dicbp)_2{}^+Cl^-]_n$, formed in a quantitative yield (on the basis of the rhodium reactant), was filtered off, washed with CH_2Cl_2 (200 mL), and then vacuum-dried (80 °C (0.1 torr)). Anal. Calcd for $C_{28}H_{16}N_4ClRh$: C, 61.48; H, 2.93; N, 10.25; Cl, 6.49; Rh, 18.84. Found: C, 61.53; H, 3.35; N, 10.24; Cl, 5.99; Rh, 18.88. This polymer neither melts nor decomposes below 300 °C. The powder X-ray diffractometric trace data for this polymer are furnished in Table I.

Table I. Powder X-ray Diffraction Angles (θ, Deg), Interplanary Spacings (Å), Sin^2 θ Ratio Terms, and Assigned Indices for the New Hexagonal Polymer[a]

θ [θ_{calcd}[b]]	d	N_{exptl}[c] [N_{theor}[d]]	assigned indices h	k	l
1.69 [1.69]	26.12	1 [1]	1	0	0
2.93 [2.92]	15.07	3.00 [3]	1	1	0
3.37 [3.38]	13.10	3.97 [4]	2	0	0
5.05 [5.07]	8.75	8.91 [9]	3	0	0
5.85 [5.86]	7.56	11.94 [12]	2	2	0
6.07 [6.10]	7.28	12.85 [13]	3	1	0
6.77 [6.77]	6.53	15.98 [16]	4	0	0
8.47 [8.48]	5.23	24.94 [25]	5	0	0
8.97 [8.98]	4.94	27.95 [28]	4	2	0
9.45 [9.45]	4.69	30.99 [31]	5	1	0
10.18 [10.19]	4.36	35.94 [36]	6	0	0
11.80 [11.78]	3.77	48.08 [48]	4	4	0
12.27 [12.28]	3.62	51.93 [52]	6	2	0
12.56 [12.57]	3.54	54.37[e]	0	0	1
12.71 [12.68]	3.50	55.66[e]	1	0	1
12.89 [12.91]	3.45	57.22[f]	1	1	1
12.89[g] [12.86]	3.45	57.22[f] [57]	7	1	0
13.02 [13.03]	3.42	58.36[e]	2	0	1
13.58 [13.58]	3.28	63.39[f]	3	0	1
13.58[g] [13.65]	3.28	63.39[f] [64]	8	0	0
14.29 [14.33]	3.12	70.05[e]	4	0	1
15.55 [15.53]	2.87	82.65[e]	4	2	1

[a] Space group $P6$: cell dimensions $a(=b) = 30.16$ Å, $c = 3.54$ Å. [b] Calculated from $\sin^2\theta(hkl) = A(h^2 + hk + k^2) + Cl^2$, where $A = \lambda^2/3a^2$ and $C = \lambda^2/4c^2$. [c] $N_{exptl} = \sin^2\theta(hk0)/\sin^2\theta(100)$. [d] $N_{theor} = h^2 + hk + k^2$. [e] Differs slightly from the nearest N_{theor} term. [g] And/or.

$[Ir(dic)_2{}^+Cl^-]_n$ Polymers. A general procedure for the preparation of the iridium polymers involves the dropwise addition of a CH_2Cl_2 solution (50 mL) of the diisocyanide (~1.0 mmol) into a magnetically stirred solution of $[IrCl(cod)]_2$ (0.15 g, 0.23 mmol) in the same solvent (25 mL) at ambient temperature (~25 °C). The gray-brown precipitates of the products formed during the course of these reactions were filtered off, extensively washed with CH_2Cl_2, and then vacuum-dried at 80 °C (0.1 torr). The new polymeric products, which were characterized as $[Ir(dic)_2{}^+Cl^-]_n$, are formed in a quantitative yield with respect to the starting iridium complex. The elemental compositional data of the iridium polymers are as follows. Anal. Calcd for the 1,4-diisocyanobenzene polymer ($C_{16}H_8N_4ClIr$): C, 39.70; H, 1.65; N, 11.58; Cl, 7.23; Ir, 39.74. Found: C, 39.80; H, 1.90; N, 11.34; Cl, 6.98; Ir, 39.92.

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Calcd for the 1,3-diisocyanobenzene polymer ($C_{16}H_8N_4ClIr$): C, 39.70; H, 1.65; N, 11.58; Cl, 7.33. Found: C, 39.75; H, 3.12; N, 11.73; Cl, 6.83.

Calcd for the 2,4-diisocyanotoluene polymer ($C_{18}H_{12}N_4ClIr$): C, 42.20; H, 2.34; N, 10.94; Cl, 6.93. Found: C, 42.21; H, 2.43; N, 11.02; Cl, 6.90.

Calcd for the 4,4′-diisocyanobiphenyl polymer ($C_{28}H_{16}N_4ClIr$): C, 52.86; H, 2.52; N, 8.81; Cl, 5.58. Found: C, 52.66; H, 3.40; N, 8.73; Cl, 4.97.

Calcd for the 4,4′-diisocyanodiphenylmethane polymer ($C_{30}H_{20}N_4ClIr$): C 54.40; H, 3.01; N, 8.44; Cl, 5.34. Found: C, 52.49; H, 3.15; N, 8.02; Cl, 5.42.

Calcd for the 1,5-diisocyanonaphthalene polymer ($C_{24}H_{12}N_4ClIr$): C, 49.34; H, 2.06; N, 9.59; Cl, 6.07. Found: C, 49.25; H, 2.55; N, 9.60; Cl, 5.86. These iridium(I) polymers neither melt nor decompose below 300 °C. Their spectroscopic and structural properties are discussed in the text.

Results and Discussion

Hexagonal Modification of $[Rh(dicbp)_2{}^+Cl^-]_n$. The reaction of $[Rh(CO)_2Cl]_2$ with 4,4′-diisocyanobiphenyl has been reported[1] to give a two-dimensional coordination polymer of the type $[Rh(dicbp)_2{}^+Cl^-]_n$ with stacked layers and a tetragonal structure. A second structural modification of the same empirical formula has been realized when this reaction was carried out under slightly different conditions. The formation of the new hexagonal (H) modification has been observed to be favored with a diisocyanobiphenyl to $[Rh(CO)_2Cl]_2$ molar ratio greater than 8, whereas the tetragonal (T) polymer is preferred with a lower reactants ratio. Even under these experimental conditions in CH_2Cl_2 at ambient temperature, both modifications do occasionally form simultaneously. Though both polymers T and H can now be prepared in a relatively pure state, the reasons why such entirely different structural modifications are formed under rather similar experimental conditions are not immediately apparent.

Visual distinction between the two modifications is possible since the dark green, almost black, color of T differs from the bright green color of H. The isocyanide stretching frequencies [ν(NC)] in the infrared spectra of both polymers appear at about the same position (2135 ± 5 cm^{-1}). The presence of a single strong ν(NC) band in each spectrum does suggest the existence of ordered polymeric networks. The diffuse-reflectance spectrum of H shows absorptions centered at 425 (23 529) and 690 nm (14 493 cm^{-1}), which are slightly red shifted compared with those reported for T [410 (24 390) and 660 nm (15 152 cm^{-1})]. In both spectra, the low-energy band appears in a region (visible) characteristic of weak intrachain Rh–Rh interactions. Distinction between the two modifications is best achieved from their powder X-ray diffractometric traces. Comparison of the five diffraction angles reported[1] for T (2.91, 4.12, 5.84, 8.77, and 11.73°) shows that the well-resolved trace of H consists of some 20 unique reflections (Table I). This technique can be viewed as the best method to distinguish between the T and H modifications. Besides its application as a qualitative diagnostic tool, powder X-ray diffraction data may also be used for structural assignment, an issue to be discussed later.

The presumed polymeric nature of both the T and H modifications is consistent with their elemental composition data since the retention of the local square-planar symmetry around the rhodium(I) (d^8) necessitates the presence of two diisocyanobiphenyl ligands per metal atom, as was found. The spatial arrangement of the T modification has previously[1] been suggested to consist of two-dimensional rigid $[Rh(bridge)_2]_n$ networks stacked on top of each other in an eclipsed fashion via weak intrachain Rh(I)···Rh(I) interactions. The X-ray diffraction pattern of this modification was found to be consistent with the presence of a tetragonal rhodium atom system. Structural information concerning the polymeric matrix in H was also obtained by an X-ray diffraction study. In the absence of suitable single crystals, the structure of this polymer was resolved by the use of the powder X-ray diffractometric trace data (Table I) and a viable model system. A schematic presentation of the two-dimensional propagation model of the $[Rh(bridge)_2]_n$ network in the H polymer is shown in Figure 1. A confined section of the two-dimensional molecular model with the unit cell is shown in Figure 2. The molecular model was constructed by using conventional bond distances similar to those found in related rhodium complexes[7,8] and idealized bond angles except in the instances of Rh–C–N and C–N–C where off-linearity was allowed in order to attain a bridge span of 15.15 Å, a distance previously characterized[1] in the T polymer. The phenyls of the biphenyl units are presumed to be perpendicular and to intercept the molecular plane with a 45° angle. The model-calculated cell dimension is $a(=b) = 30.30$ Å. The spatial arrangement of the H polymer may be derived by the eclipsed stacking of the two-dimensional model via weak intrachain Rh(I)···Rh(I) interactions, a process which is consistent with the established tendency of the $Rh(CNR)_4{}^+$ cations to oligomerize.[7,9,10]

Interpretation of the powder X-ray diffraction data (Table I) in terms of reflections originating from Rh-containing sets of planes appears to be consistent with the presence of rhodium atoms arranged in a hexagonal system.[11] The first diffraction

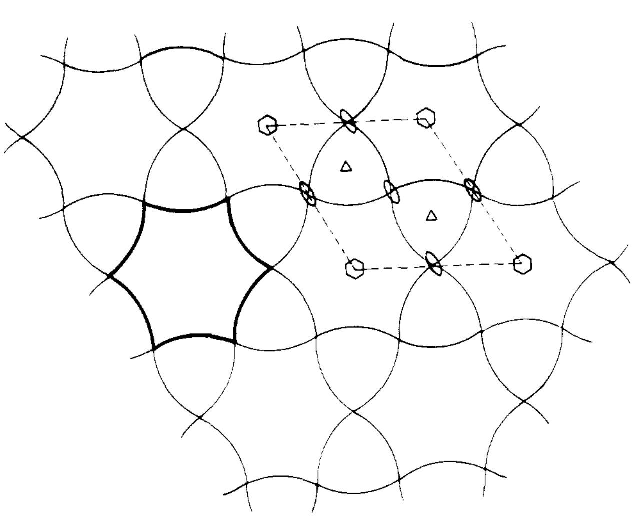

Figure 1. Schematic presentation of the two-dimensional propagation model of the $[Rh(dicbp)_2]_n$ network in the hexagonal polymer (H).

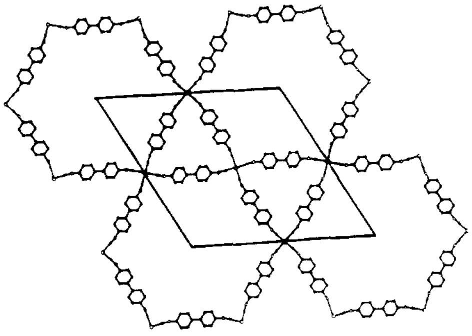

Figure 2. Two-dimensional molecular model of the unit cell [$a(=b) = 30.16$ Å] of the hexagonal rhodium polymer (H).

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angle in the trace (1.69°) was assigned to the 100 planes. Other *hk*0 diffractions were identified by considering the N_{exptl} and N_{theor} terms, according to an established procedure. The first diffraction not belonging to the *hk*0 family, found at 12.56°, was assigned to the 001 planes, and this corresponds to Rh(I)···Rh(I) distances [*d*(001)] of 3.54 Å. This assignment is complemented by the presence of other *hk*1 diffractions (101, 111, 201, 301, 401, and 421) which were identified by the comparison between the experimental (θ) and calculated (θ_{calcd}) angles (Table I). The data presented in Table I are convincingly consistent in the framework of a hexagonal system. For instance, the experimental cell dimension (*a*) derived from *d*(100)/sin 60° [=30.16 Å] is in close agreement with the value 30.14 Å obtained from *d*(110). Likewise, implication of the experimental cell dimensions $a(=b) = 30.16$ Å and $c = 3.54$ Å in the computation of the θ_{calcd} terms (Table I) give calculated angles which are within experimental error (±0.03°) of the trace measured data points (θ). The similar bridge spans found in the T (15.15 Å)[1] and H (15.08 Å) modifications are significantly shorter compared with the idealized term (16.07 Å) which pertains to a perfectly collinear span. The off linearity of the Rh–C–N and C–N–C bonds in the H polymer may be estimated (19.43°) by the crude assumption that both angles are identical.[12]

Interpretation of the powder X-ray diffraction data of H in terms of a specific model leads to an obvious question concerning alternative structures. The origin of the diffraction pattern from a hexagonal rhodium atom system is almost certain, and this when considered in the context of terminally coordinated stereochemically rigid diisocyanide linkages rules out any reasonable structural alternatives. In the existing model, the powder X-ray diffraction data support the presence of the hexagonal $[Rh(bridge)_2]_n$ network. The positions of neither the chloride counterion nor the water molecules in the hydrated H polymer $[Rh(dicbp)_2{}^+Cl^-\cdot xH_2O]_n$ could be determined from available powder X-ray diffraction data. The rigorously dried polymer is rather hydroscopic and absorbs water on standing in air.

The presence of an extensive network of weak Rh(I)···Rh(I) bonding interactions in the H polymer is of interest. Intrachain metal–metal distances found in the H polymer are significantly longer than those reported for the dinuclear cations $[Rh_2(CNAr)_8]^{2+}$ [Ar = phenyl (3.19 Å),[7] 4-fluorophenyl (3.21 Å),[8] and 4-nitrophenyl (3.25 Å)[8]] and $[Rh_2(CNCH_2CH_2CH_2NC)_4]^{2+}$ (3.26 Å).[13] Distances which are even shorter have been characterized in certain chloro-bridged neutral dinuclear complexes such as $[RhCl(CO)(PMe_2Ph)]_2$ (3.17 Å)[14] and $[Rh(CO)_2Cl]_2$ (3.12 Å).[15] A more appropriate comparison between the H polymer and an extended series of related tetragonal polymers of the type $[Rh(bridge)_2{}^+Cl^-]_n$ [e.g., bridge = 1,4-diisocyanobenzene (3.31 Å),[1] 1,4-diisocyanonaphthalene (3.39 Å),[3] 1,5-diisocyanonaphthalene (3.41 Å),[3] and 4,4′-diisocyanodiphenylmethane (3.39 Å)[2]] reveals more compatible metal–metal distances, as might have been expected. In contrast with the discrete, nonetheless isolated, Rh(I)···Rh(I) interactions found in dinuclear complexes, metal–metal interactions in the H and T polymers proceed via columnar stacking, a situation commonly described as a one-dimensional metal in the terms of the low-dimensional cooperative phenomena.[16] Interactions between adjacent Rh(I) atoms in the columnar metal chains are expected to be somewhat weaker than those found in discrete dinuclear complexes since in the former instance both axial positions of each metal are engaged in bonding interactions. This feature manifests itself in the above considered metal–metal distances.

The electronic spectra of H is rather similar to that already reported[1] for the T modification. In the visible region, the center of the extended absorption envelope found in the spectrum of H is slightly red shifted as compared with that of T. Interpretation of the spectrum of H in terms of a band diagram similar to that derived[1] for T is quite appropriate. The visible absorption of H corresponds, most probably, to a multitude of electronic transitions occuring between the upper region of the *bonding* and lower region of the *antibonding* bands. The presence of such band gap transitions, which originate from weak metal–metal bonding interactions, is consistent with the characterization of relatively long intrachain Rh(I)···Rh(I) distances in H.

Despite their identical empirical formula, the structural features of the hexagonal (H) and tetragonal (T)[1] polymers differ rather substantially from each other. The triangular sections in the H polymer are the source of considerable structural constrain which is offset, in part, by the systematic bending of the Rh–C–N–C bridge angles. Perfectly collinear bridge spans would have required interligand angles of 60 (triangles) and 120° (hexagonals), namely, a substantial distortion of the preferred square-planar symmetry at the rhodium(I) (d^8) sites. By contrast, there appears to be little, if any, constraint associated with the structures of the tetragonal (T) polymers. Indirect evidence in support of a constrained hexagonal (H) modification has been obtained by the observation of an unusual pressure-induced H → T transformation. The powder X-ray diffractometric traces of compressed powder pellets of the H polymer reveal a pressure-dependent transformation which begins below a pressure of 2 tons cm^{-2}. This transformation is essentially completed when the pellets are compressed at 25 tons cm^{-2} for a brief period of 60 s. Since the diffractometric traces of the H and T polymers differ rather substantially from each other, the transformation process could be followed rather easily. A change from H to T necessitates the breaking and reforming of coordination bonds between the rhodium atoms and diisocyanobiphenyl ligands; therefore, this process cannot be viewed as a pressure-induced phase transition. This transformation is probably best characterized as a solid-state isomerization process by which the triangular ring strain in the H polymer is released during the formation of the thermodynamically preferred T modification. The mechanistic aspects of this process are not immediately apparent.

$[Ir(dic)_2{}^+Cl^-]_n$ Polymer. The collinear (1,4-diisocyanobenzene (dib) and 4,4′-diisocyanobiphenyl), bent (1,3-diisocyanobenzene, 2,4-diisocyanotoluene, and 4,4′-diisocyanodiphenylmethane), and parallel (1,5-diisocyanonaphthalene) diisocyanides under study have been observed to undergo a facile reaction with $[IrCl(cod)]_2$ to afford insoluble products of the type $[Ir(dic)_2{}^+Cl^-]_n$. The polymeric nature of these products may be suggested from the ligand to iridium (or chloride) ratio which is expected to be 2 for an infinitely large ($n \rightarrow \infty$) polymeric matrix. The iridium(I) polymers are virtually insoluble in both aqueous and organic media, and unless rigorously dried under vacuum, they are best formulated as $[Ir(dic)_2{}^+Cl^-\cdot xH_2O]_n$ (x = 0–3). Routine purification

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[12] This angle was calculated from the equation $2A\cos^2\alpha + B\cos\alpha - (A + C) = 0$, where A = d[Rh–C] (1.94 Å), B = d[(Rh)C–N] (1.15 Å), and $C = A + B - D$. The term D (0.495 Å) represents half of the difference between the ideal (16.07[1]) and experimental (15.08) bridge span (Å).

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[15] Dahl, L. F.; Martell, C.; Wampler, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 1761–1768.

[16] Keller, H. J., Ed. "Low-Dimensional Cooperative Phenomena—The Possibility of High-Temperature Superconductivity"; Plenum Press: New York and London, 1979; and pertinent chapters therein discussing various aspects of one-dimensional metals.

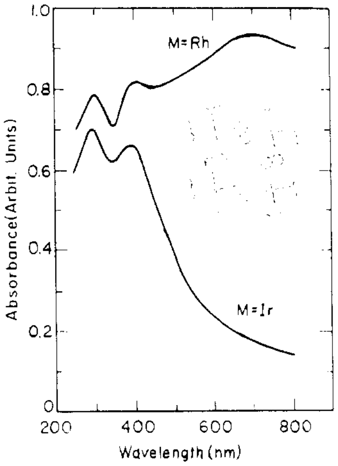

Figure 3. Diffuse-reflectance spectra of the $[M(dicn)_2{}^+Cl^-]_n$ (dicn = 1,5-diisocyanonaphthalene) polymers of M = Rh (top) and Ir (bottom) and a two-dimensional model of their $[M(bridge)_2]_n$ network.

techniques of complexes such as recrystallization and/or sublimation are not applicable for these polymers. These properties made it rather difficult to obtain perfect sets of elemental composition data for all of the polymers.

The infrared spectra of the iridium polymers, taken as KBr pellets, exhibit one strong ν(NC) band at 2122 ± 18 cm^{-1} that is characteristic of terminally coordinated isocyanides[17] in a symmetric environment. The diffuse-reflectance spectra of these polymers do not show absorptions in the visible region, and this may signify the absence of columnar iridium(I) chains. This feature is best exemplified from the comparison between the diffuse-reflectance spectra of the analogous rhodium and iridium polymers of 1,5-diisocyanonaphthalene which are shown in Figure 3. Three-dimensional order in the iridium polymers could result from either metal–metal interactions, as in the case of the rhodium polymers, or crystal-packing forces. The loss of order in just one-dimension may be inferred from powder X-ray crystallography by the detection of fewer diffraction lines of greater width. The powder X-ray diffraction pattern of $[Ir(dib)_2{}^+Cl^-]_n$ was determined with both a diffractometric trace technique [θ, broad band in the range 3.6–6.0°] and a Debye–Scherrer photograph [θ, broad line in the range 3.5–5.5°] and compared with that of the analogous rhodium polymer [θ, 3.85 (100), 5.30 (110), 7.80 (200), and 13.48° (001)],[1] in which the metal atoms assume a tetragonal geometry. Since the rigid bridge span distances in both polymers are expected to be similar in magnitude, the single broad diffraction line observed for the iridium polymer most probably originates from the mixing of reflections coming from the 100 and 110 planes of a two-dimensional ordered network.

The two-dimensional order of the iridium(I) polymers may be assigned by analogy with the respective rhodium polymers for which structural data are available. Linear, or nearly linear, translation of the D_{4h} coordination sphere of the iridium(I) (d^8) atom with 1,4-diisocyanobenzene, 4,4′-diisocyanobiphenyl, and 1,5-diisocyanonaphthalene should dictate the formation of genuine two-dimensional polymers. This, however, is not a strict requirement with the bent bridging ligands (1,3-diisocyanobenzene, 2,4-diisocyanotoluene, and 4,4′-diisocyanodiphenylmethane) where propagation may proceed other than in two dimensions.

The iridium polymers undergo facile oxidative addition reactions with halogens (X_2), for example, to afford oxidized polymers of the type $[Ir(bridge)_2X_2{}^+Cl^-]_n$. The IR spectra of the oxidized polymers show one strong ν(NC) band at a frequency 30–50 cm^{-1} higher than that found in the spectra of the parent polymers, as was expected.[17] It is pertinent to point out that both the parent and oxidized polymers give similar diffuse-reflectance spectra in the visible range, and this may provide further circumstantial support for the absence of any metal–metal bond-breaking processes during the course of the oxidative-addition reactions. In contrast with these findings, the absorptions in the visible range of the analogous rhodium(I) polymers are greatly affected after such oxidative-addition reactions.[1]

The absence of intrachain metal–metal interactions in the iridium(I) polymers may be suggested on the basis of the experimental results so far considered. This observation is rather surprising in light of the pronounced ability of related iridium(I) complexes to undergo stacking via intrachain Ir(I)···Ir(I) interaction. Linear-chain iridium carbonyl halides[18,19] and oligomers of the type $[Ir(CNR)_4]_n{}^{n+}$ (e.g., R = Ph[20] and Me[21]) are several examples among many where this tendency has been characterized. In isostructural and isoelectronic analogues of the type $[M(acac)(CO)_2]_n$ (M = Rh, Ir),[22,23] Rh–Rh bonds (3.26 Å) are significantly longer than the corresponding Ir–Ir bonds (3.20 Å),[23] and this suggests stronger bonds in systems of the third-row d-block elements. In the instance of $[M(CN\text{-}t\text{-}Bu)_4]_n{}^{n+}$ (M = Rh,[7] $n \geq 1$; M = Ir,[21] $n = 1$), the results may suggest a greater tendency of oligomerization for the rhodium rather than the iridium system. In view of the foregoing, it would appear rather difficult at this point to suggest an overall rationale for our experimental findings concerning the relative tendency of stacking of the rhodium(I) and iridium(I) polymers.

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Registry No. $[Rh(dicbp)_2{}^+Cl^-]_n$, 74620-95-4; $[Ir(1,4\text{-}dicb)_2{}^+Cl^-]_n$, 79721-92-9; $[Ir(1,3\text{-}dicb)_2{}^+Cl^-]_n$, 79721-94-1; $[Ir(dict)_2{}^+Cl^-]_n$, 79721-96-3; $[Ir(dicbp)_2{}^+Cl^-]_n$, 79721-98-5; $[Ir(dicdpm)_2{}^+Cl^-]_n$, 79723-26-5; $[Ir(dicn)_2{}^+Cl^-]_n$, 79721-90-7; $[Rh(CO)_2Cl]_2$, 14523-22-9; $[IrCl(cod)]_2$, 12112-67-3.

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