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Vibrational Spectroscopic Investigation of Rigid-Rod Platinum σ-Acetylide Polymers Containing Variable Acetylenic Microstructures

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A detailed study of the vibrational spectra of the rigid-rod Pt(II)−σ-acetylide polymers, $[(P^nBu_3)_2Pt-C\equiv CC\equiv CC\equiv C-]_n$, $[(P^nBu_3)_2Pt-C\equiv CC\equiv C-]_n$, $[(P^nBu_3)_2Pt-C\equiv CC_6H_4C\equiv C-]_n$, $[(P^nBu_3)_2Pt-C\equiv CC\equiv CC_6H_4C\equiv CC\equiv C-]_n$, and $[(As^nBu_3)_2Pt-C\equiv CC_6H_4C\equiv C-]_n$ is reported. The backbone chain vibrations in these highly conjugated organometallic polymers can be analyzed by relating them to their centrosymmetric monomeric structures with an approximate C_{2h} or D_{2h} local symmetry. The extent of π-conjugation in the backbone can be monitored from the associated changes in the vibrational frequencies, in particular, the $\nu_{C\equiv C}$ modes. In general, the vibrational spectra of the polymers suggest that the backbone is essentially alternating $-C\equiv C-$ in nature, without any contribution from allene-type structures ($=C=C=$). The interruption of the acetylenic linkages with phenyl groups reduces the π-conjugation. The near-infrared FT-Raman spectra of the polymers show resonance enhancement of selected vibrations which occur along the direction of the polymer chain, presumably due to coupling with electronic transitions of the backbone. In addition, these polymers exhibit strong and substituent-sensitive fluorescence in their FT-Raman spectra.

Introduction

Rigid-rod organometallic polymers containing transition metal fragments linked with acetylenic chromophores in the backbone continue to attract much attention due to their potential applications as new materials for third-order nonlinear optics, liquid crystal, and conductivity devices.[1−4] This is largely attributed to their linear backbone structure which supports extended π-conjugation. Various transition metals from groups 8−10 (Fe, Ru, Co, Rh, Ni, Pd, Pt) and different alkynyl structures have been introduced into the polymer backbone[4−7] to enhance metal dπ−pπ* back-bonding, which is expected to contribute significantly to the π-electron delocalization in these polymers. An evaluation of such delocalization can be made from the $\nu_{C\equiv C}$ stretching modes, which shift to lower energies upon alkyne-to-allene type structural changes. Vibrational spectroscopy has been used extensively to characterize transition metal σ-acetylide complexes. To our knowledge, however, there is no discussion of the IR and Raman spectra in the literature which provides a qualitative evaluation of the electronic structure of such polymers. In our continuing efforts to understand structure−property relationships in these types of polymers, we report here the results of a detailed study of the vibrational spectra of five Pt(II)−σ-acetylide poly-

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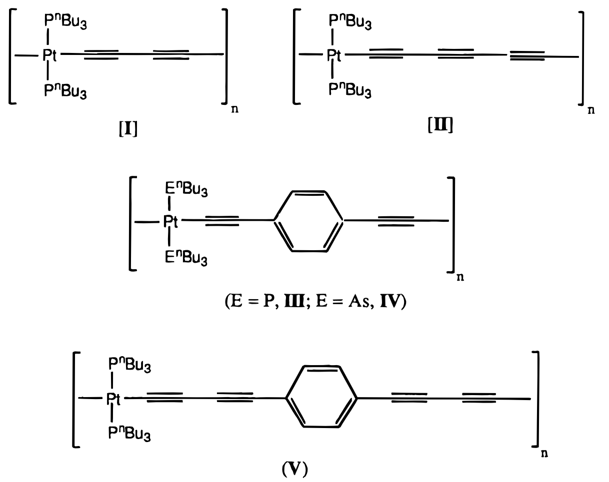
Chart 1



[I] [II]

(E = P, **III**; E = As, **IV**)

(**V**)

mers (**1-V**) (see Chart 1), in which the alkynyl structure has been varied to determine the extent of π-electron delocalization and the effect of incorporating phenyl groups in between alkynyl units linked to metal centers.

Experimental Section

The synthesis and full characterization including molecular weight determinations of the polymers studied here, $[-\mathrm{Pt}(\mathrm{P^nBu_3})_2(\mathrm{C{\equiv}C})_x-]_n$ (x = 2, 3; **I**, **II**) and $[-\mathrm{Pt}(\mathrm{E^nBu_3})_2\text{-}(\mathrm{C{\equiv}C})_x\text{-}p\text{-}\mathrm{C_6H_4}(\mathrm{C{\equiv}C})_x-]_n$ (E = P, x = 1, 2; E = As, x = 1; **III**–**V**), have been described in detail earlier.[6d] The polymers are yellow or yellow-orange amorphous powders.

Solid-state IR spectra were recorded at 0.5 cm^{-1} nominal resolution (~1000 scans) on a Bruker IFS-48 FT-IR spectrometer using the Bruker A-590 infrared microscope equipped with a liquid N$_2$-cooled mercury cadmium telluride detector. The samples were placed on a 0.5 cm thick KBr plate and observed in the transmission mode. Solution IR spectra were recorded at 2 cm^{-1} nominal resolution in the macro chamber of the same instrument using the standard deuterium triglycine sulfate detector supplied. FT-Raman spectra, induced by near-IR laser irradiation at 1064.1 nm from an air-cooled Nd^{3+}:YAG laser operating routinely at ~280 mW power, were recorded in 180° scattering mode at 2.6 cm^{-1} nominal resolution (~2000 scans) using a Bruker IFS-88 FT-IR spectrometer coupled to a Bruker FRA-105 FT-Raman module equipped with a liquid N$_2$-cooled proprietary detector. The samples were packed neat in the standard sample cups supplied with the instrument.

Results and Discussion

The solid-state IR spectra measured for the organometallic polymers **I-V** in the present study (Figure 1, Table 1) are very similar to the solution spectra reported earlier,[6d] with the exception of that of the pseudotetraacetylenic polymer (**V**). In this case, there are two acetylenic C≡C stretching bands at 2181 and 2057 cm^{-1}, with the one at lower energy having considerably lower intensity than the other. A re-examination of the IR spectrum of **V** in dichloromethane solution did reveal a weak IR peak at 2058 cm^{-1}, partially obscured by a weak solvent band. The small solvent effect on the IR bands (the solid-state band positions are in general ~2 cm^{-1} different from the solution values) indicates a limited solvent interaction with the polymers.

Apart from the acetylenic C≡C stretching vibrations, the IR spectra are dominated by the vibrations due to the ancillary ligands (P^{n}Bu$_3$, As^{n}Bu$_3$), particularly when the polymer backbones do not contain a phenylene group (**I**, **II**). These ancillary ligand vibrations do not change significantly in position or intensity in the spectra of the polymers, even upon substitution of arsenic for phosphorus. Several bands have been left unassigned in Table 1, despite being relatively strong, and these may be due to overtone or combination bands or perhaps are components of the wagging and deformation modes of the CH$_2$ and CH$_3$ vibrations surrounding them. Other chain group vibrations which appear in these spectra are those of the phenyl rings in compounds **III**–**V**, in particular, the weak bands at 1600 cm^{-1} and the strong semicircle stretches at ~1500 cm^{-1}. The 1600 cm^{-1} band is of particular interest as the vibration to which it would normally be assigned is strictly IR forbidden. Also, it is known that the slightly lower frequency component of this vibration at ~1580 cm^{-1} is sensitive to ring conjugation.[8] Other prominent bands are those at ~900 cm^{-1} belonging to the phenyl group C–H wagging vibrations. In the compounds containing linked acetylene groups (–C≡CC≡C–: **I**, **II**, and **V**), there is a band near 800 cm^{-1}, which appears characteristic of this functional group and may be due to the ≡CC≡ stretching motions.[8]

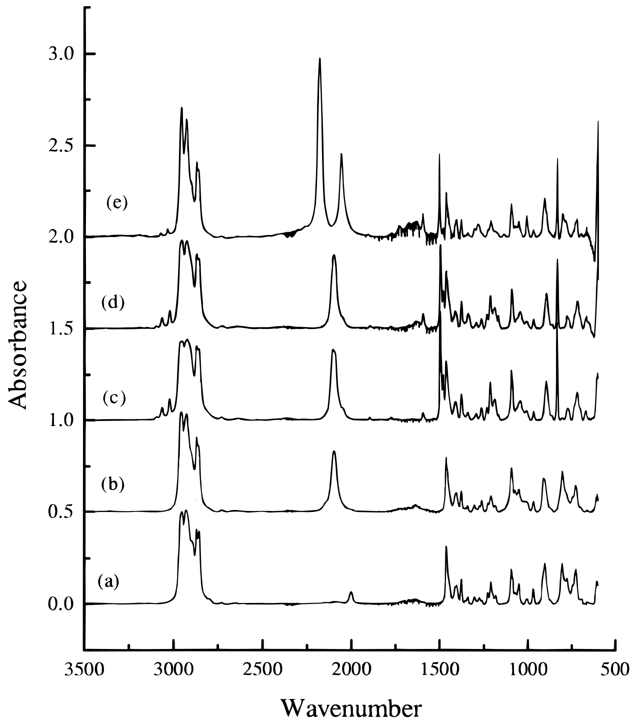


Figure 1. FT-IR spectra of (a) $[(\mathrm{PBu_3})_2\mathrm{Pt}{-}\mathrm{C{\equiv}CC{\equiv}C}{-}]_n$, (b) $[(\mathrm{PBu_3})_2\mathrm{Pt}{-}\mathrm{C{\equiv}CC{\equiv}CC{\equiv}C}{-}]_n$, (c) $[(\mathrm{PBu_3})_2\mathrm{Pt}{-}\mathrm{C{\equiv}CC_6H_4C{\equiv}C}{-}]_n$, (d) $[(\mathrm{AsBu_3})_2\mathrm{Pt}{-}\mathrm{C{\equiv}CC_6H_4C{\equiv}C}{-}]_n$, and (e) $[(\mathrm{PBu_3})_2\mathrm{Pt}{-}\mathrm{C{\equiv}CC{\equiv}CC_6H_4C{\equiv}CC{\equiv}C}{-}]_n$. Spectra are normalized such that the ν(C–H) bands due to the ancillary ligand methyl group symmetric stretch are of the same absorbance value.

The extent of π-conjugation along the chain should be reflected in the C≡C stretching frequencies. Values reported here are well within the range observed for a broad selection of monomeric,[9–19] dimeric,[20] and poly-

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Table 1. Infrared and Raman Spectra of Rigid-Rod Polymers

	I		II		III		IV		V	
assgnt[a]	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman
ν_{C-H} b_g						3187(16)		3190(17)		
ν_{C-H} a_u					3097(5)		3098(5)		3105(1)	
ν_{C-H} a_g						3051(23)		3050(25)		
ν_{C-H} b_u					3065(17)		3065(16)		3072(4)	
ν_{C-H} b_u					3023(29)		3023(26)		3033(10)	
CH_3 ν_{C-H} as	2964(95)	2957(50)	2964(116)	2959(62)	2968(89)	2957(80)	2966(116)	2955(78)	2958(172)	2962(42)
CH_3 ν_{C-H} as	2952(137)		2953(122)		2953(107)		2952(115)			
CH_2 ν_{C-H} as	2933(79)	2933(116)	2935(69)	2934(123)	2928(176)	2934(118)	2931(94)	2935(115)	2928(157)	2938(118)
CH_2 ν_{C-H} as	2918(65)		2921(65)							
Fermi res	2892(281)	2898(64)	2898(207)	2906(162)	2903(94)	2906(190)	2907(181)	2909(176)	2904(207)	2901(153)
CH_3 ν_{C-H} s	2870(100)	2870(100)	2872(100)	2874(100)	2872(100)	2874(100)	2872(100)	2872(100)	2871(100)	2874(100)
CH_2 ν_{C-H} s	2856(97)	2858(89)	2859(88)		2857(95)	2859(79)	2858(94)	2859(82)	2859(91)	2862(84)
$\nu_{C\equiv C}$ a_g		2140(1485)		2136(3399)		2104(2756)		2104(2193)		2176(7940)
$\nu_{C\equiv C}$ a_u/b_{3u}	2002(17)		2098(81)		2103(93)		2098(94)		2181(234)	
$\nu_{C\equiv C}$ a_g										2065(370)
$\nu_{C\equiv C}$ a_u/b_{3u}				2000(1306)					2057(108)	
ν_{C-C} a_g					1595(11)	1597(2488)	1595(22)	1597(2035)	1596(31)	1597(4440)
ν_{C-C} b_u					1497(136)		1497(111)		1503(118)	
					1481(68)		1480(54)		1482(21)	
$\delta_{as}CH_3$	1465(78)		1465(74)		1465(87)		1465(80)		1465(70)	
δ_{CH_2}	1458(60)	1452(34)	1460(59)	1455(29)	1458(69)	1451(23)	1458(65)	1451(34)	1456(43)	
scissor	1445(33)	1447(45)	1444(29)	1446(27)	1448(40)	1447(38)	1446(39)	1448(34)	1447(25)	
δ_{P-CH_2}	1415(28)	1409(22)	1417(24)	1412(13)	1413(32)	1416(13)	1413(30)	1415(15)	1411(23)	
	1403(29)		1406(27)		1403(27)	1405(9)	1403(26)	1405(11)	1404(27)	
δ_s CH_3	1378(38)		1378(30)		1378(41)		1378(43)		1378(26)	
ρ_t CH_2		1305(30)		1306(18)		1293(9)		1292(11)		
ν_{C-X} a_g						1220(232)		1220(184)		1296(740)
β_{C-H} (2,5 vs 3,6)						1170(1172)		1170(986)		1177(1400)
C−C−C str.	1094(49)	1099(23)	1094(60)	1096(19)	1093(65)	1095(11)	1093(52)	1093(12)	1095(116)	1099(70)
+$CH_{2\ wag}$	1086(38)	1068(44)					1086(30)		1086(32)	
	1051(33)	1053(36)	1051(29)	1052(29)	1045(26)	1052(22)	1045(25)	1055(17)	1052(24)	1051(20)
unassigned										1022(220)
unassigned		971(19)								988(170)
unassigned	970(15)		969(6)		968(15)		968(11)		968(9)	
C−C−C str.	913(42)		913(44)						913(37)	
+	904(34)		904(42)		896(50)		898(39)		904(47)	
CH_3 rock	894(35)	893(26)	895(27)	896(12)	884(26)	892(25)	891(42)	891(22)	893(30)	
unassigned		865(19)		867(11)		864(20)		863(17)		
αC−C−C ag **quadrant ip.**						838(167)		838(128)		
γ_{C-H} b_u ad_j					835(120)		833(120)		833(107)	
H wag					834(90)					
$\beta_{\equiv CC\equiv}$ b_u	807(52)		805(55)						803(34)	
unassigned	777(34)		778(26)		777(18)		778(17)		782(23)	
unassigned					767(15)		767(12)			
unassigned	745(26)		746(22)		737(20)		735(18)		738(10)	
$CH_{2\ rock\ ip}$	727(43)		726(37)		719(36)		718(36)		722(24)	
ϕ_{C-C} a_g oop sextant						725(33)		726(27)		722(10)
unassigned	694(6)		700(7)		700(14)		702(16)			
unassigned					670(12)		668(11)			
α_{C-C-C} b_g quadrant ip.						653(34)		653(34)		
$\beta_{C-C\equiv C}$ b_g						549(100)		550(88)		527(15)
M−C str.		484(185)		486(183)		474(74)		475(66)		496(201)
unassigned										423(190)

[a] Assignments according to refs 8, 41, 42, and 43. Intensities (in parentheses) measured relative to higher component of methyl ν_{C-H} symmetric. Assignments in bold face are in-chain vibrations.

meric[5,21,22] complexes of nickel, palladium, and platinum. In a series of related monomeric ruthenium σ-acetylide complexes,[9] the IR frequencies of the $\nu_{C\equiv C}$ bands are related to the observed acetylenic bond lengths. The frequencies of these vibrations are more representative of acetylene units than those of cumulated allene type moieties. Thus, a single/triple bond alternation most accurately reflects the structure of the polymer backbone. This is also true of organic materials with nonuniform conjugated π-systems, such as phenyl acetylenes,[23,24] even in extended systems.

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Increased π-conjugation reduces the C≡C vibrational frequency, because the triple bond character of individual units is reduced (consequently reducing the bond strength of the acetylene links). There is a significant frequency decrease upon coordination; however, further reduction in $\nu_{C\equiv C}$ upon polymerization is small.

The $\nu_{C\equiv C}$ frequencies are considerably lower in pure poly(metallaacetylene) chains (**I**, **II**) than are those in which the acetylene moieties are spaced by phenylene groups. This difference is consistent with the observations from optical absorption and photoluminescence studies[6d] and reflects the fact that π-conjugation is greater in purely acetylenic polymer backbones. The observed acetylenic vibrations are very strong and are within the expected frequency range, except for the diacetylenic compound (**I**). This material is anomalous in several ways, not the least of which is the relatively low IR intensity of the acetylenic vibration relative to the rest of the spectrum. In Figure **1**, all the spectra are normalized such that the C−H stretching vibrations are at approximately the same intensity. The C−H stretching vibrations result mostly from motions of the ancillary ligands and, as mentioned previously, are independent of the compound. On this basis, compound **I** has a C≡C stretching band 1 order of magnitude lower in intensity than that in the other polymers. Moreover, the frequency is unusually low, possibly indicating a higher degree of π-conjugation along the chain in this material than in the others. The $\nu_{C\equiv C}$ mode (1999 cm^{-1}) is approximately 100 cm^{-1} lower than in the other compounds, closer to the high energy end of the range associated with allene species. There is no immediately apparent explanation for these phenomena, and the intensity variation is contra-intuitive, since allenes are normally stronger IR absorbers than are isolated triple bonds.[25] Intriguingly, the higher energy $\nu_{C\equiv C}$ mode at 2181 cm^{-1} for the pseudo-tetraacetylenic compound (**V**) is anomalously high in this respect, but the mean frequency (2118 cm^{-1}) of the two peaks is in the same region as that in compounds **II**−**IV**. It should also be noted that $\nu_{C\equiv C}$ for the monomeric analogue[10] is also at higher energy than in the other monomeric σ-acetylides. However, depending on symmetry considerations, some vibrational modes may not be IR active. Any analysis based on IR data alone is not necessarily complete. The complementary Raman spectra also must be considered.

Before discussing the Raman spectra or making comparisons of the IR and Raman data, it is important to examine the symmetry considerations which govern the vibrational spectra of these polymers. Generally, it is difficult to define the molecular symmetry of polymeric materials due to the extensive and variable tertiary structure to which they are subject. In the case of rigid rod polymers, however, there is a more clearly defined molecular structure. While a complete analysis of the symmetry is not feasible, a first approximation may be obtained by considering isolated polymeric subunits. In our case, each subunit may be viewed as the *n*-acetylenic or pseudo-*n*-acetylenic backbone capped by two square-planar *trans*-Pt(L)$_2$R groups (where R = the repeating polymer) (Figure 2a). Equally, this situation can be treated as a Pt-centered species with two *trans*-*n*-alkyl group V ligands and two *n*-acetylenic groups (Figure 2b). In both scenarios, the local symmetry is D_{2h}. Complexes which are effectively monomeric and dimeric units of these types have been synthesized and characterized.[10−19] The D_{2h} point group is centrosymmetric, either centered on platinum or on the center of the *n*-acetylenic chain. The same treatment applies to compounds **III**−**V**, regardless of whether the aromatic ring is fixed in the plane of the Pt(L)$_2$R$_2$ unit or perpendicular to it. For any angle between these two extremes, the point group symmetry is C_{2h}, also a centrosymmetric group. Crystallographic studies of the simple monomeric or dimeric complexes have universally shown that the latter is the case in the solid, state.[10,21,24−30] However, solid-state NMR experiments[31] have implied considerable motion within these units. No crystal data are available for the polymers or any related oligomeric species.

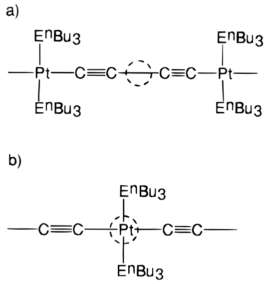

Figure 2. Two different generalized views of rigid-rod polymers, showing alternative interpretations of the symmetry: (a) Center of symmetry located halfway between two platinum atoms along the chain; (b) center of symmetry located at the platinum metal center.

The angle at which the phenylene group is tilted from the plane of the metal coordination[10,21,24−30] appears to be in the range of 30−60°. Such a variation of the phenylene group aspect has traditionally been ascribed to solid-state interactions and close contacts. However, large phenylene group rotations are common to all the reported structures, for both Ni- and Pt-centered materials. The crystal structures of related organic compounds such as 1,2-diphenylacetylene (tolane)[32] show coplanar phenyl rings. A simplistic view of the orbital overlap in these σ-acetylide complexes indicates that the energy minimum would be at a point where the rings are either coplanar with, or normal to, the plane of the metal−ancillary ligand moiety (or the other phenyl ring in the case of purely organic materials). Theoretical studies of organic materials[33] reveal minima at either[33a,b]

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or both[33c] the crystallographic orientation (coplanar rings) and perpendicular thereto. Even with a low rotation barrier, it would be expected that one of these positions would be favored over intermediate angles. It is possible that the same complicated interplay of forces that applies to the monomeric and dimeric analogues may influence the structure of the polymeric materials, a factor which may also influence the spectroscopic properties. We assume here that an angle intermediate between coplanar and normal is made for the purposes of this analysis.

For reasons of simplicity, we decided to choose the acetylene-centered description (Figure 2a) for this analysis. In addition, the metal center is something of a break point in the conjugation and therefore the acetylenic chains are somewhat vibrationally isolated within these units. The C≡C stretching vibrations, when analyzed under these assumptions, fall into three classes: the di- and pseudo-diacetylenic polymers (**I**, **III**, **IV**), the triacetylenic (**II**), and the pseudo-tetraacetylenic polymers (**V**). In the first class, two vibrations, one IR-active (A_u) and one Raman-active (A_g) are expected. In the second, three bands, one IR-active (A_u) and two Raman-active (both A_g) are symmetry implied, and in the third, two of each type are required. The number and activities of bands are the same if analyzed under D_{2h} symmetry, except that the symmetry of the IR-active bands is now B_{3u}. Here, the importance of the second, weaker IR band in compound **V** becomes clear. The IR spectra, as described, are completely in accord with this symmetry analysis. However, owing to the centrosymmetric nature of these compounds, at least half of the C≡C stretching vibrations are not observed. Comparison of the spectra of compounds **I**, **III**, and **IV** is possible because the IR bands arise from similar vibrations in each case. The IR-active bands in **II** and **V** stem from slightly different molecular motions than do those from **I**, **III**, and **IV**. Consequently, a similar comparison cannot be applied to them.

Under visible laser irradiation (514.5 nm), the polymers decompose rapidly, making conventional dispersive Raman spectroscopy impractical. On the other hand, FT-Raman spectroscopy, using near-IR 1064.1-nm laser irradiation, provides a facile and rapid entry into this aspect of the vibrational spectrum. Values for the frequencies and the proposed assignments are also presented in Table 1. The assignments were made by comparison with spectra of the related monomeric and dimeric compounds and by comparison among the polymers studied here. Intensities are measured from the white-light background corrected spectra. Several details are immediately obvious from the FT-Raman spectra (Figure 3). The spectra are offset in order to see clearly the vibrations present. Most clearly, compound **V** is anomalous in its Raman spectrum. Many peaks are either absent, considerably shifted, or very weak compared with those for the other related compounds. In complexes **I**−**V**, the most prominent features in each case are the C≡C stretching vibrations. These bands are strikingly intense, with even the weakest example (**I**) having an acetylenic stretch 1 order of magnitude stronger than the, usually strong, C−H Raman bands. In the case of the pseudo-tetraacetylenic compound (**V**), this difference is nearly 2 orders of magnitude. The overall relative intensity increases with the number of acetylene links in the repeat unit. This behavior suggests a resonance enhancement of the Raman signal. Here, this arises from electronic excitement in the near-IR by the incident laser. Although reports of near-IR resonance Raman spectra are rare, they are not unknown.[34] Optical measurements[6d] have shown considerable coupling of vibrational transitions into the electronic levels of the compounds. However, this observation is in the visible rather than in the near-IR region of the spectrum. Presumably, the electronic level involved here also results from the partially delocalized π-electrons of the acetylenic backbone. Confirmatory evidence is found in the enhanced intensity of the normally weak Pt−C stretching modes around 490 cm^{-1}. These vibrations are also mostly directed along the direction of propagation of the polymer backbone.

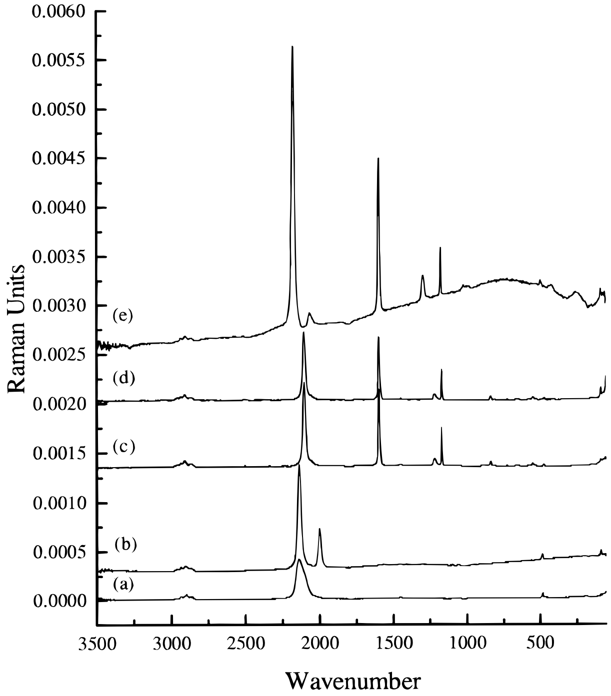

Figure 3. Near-infrared FT-Raman spectra of (a) $[(PBu_3)_2Pt{-}C{\equiv}CC{\equiv}C{-}]_n$, (b) $[(PBu_3)_2Pt{-}C{\equiv}CC{\equiv}CC{\equiv}C{-}]_n$, (c) $[(PBu_3)_2Pt{-}C{\equiv}CC_6H_4C{\equiv}C{-}]_n$, (d) $[(AsBu_3)_2Pt{-}C{\equiv}CC_6H_4C{\equiv}C{-}]_n$, and (e) $[(PBu_3)_2Pt{-}C{\equiv}CC{\equiv}CC_6H_4C{\equiv}CC{\equiv}C{-}]_n$. Spectra are normalized such that the ν_{C-H} bands due to the ancillary ligand methyl group symmetric stretch are of the same Raman intensity. The spectra are background corrected by ratio, using a white light spectrum to determine instrumental factors.

For the pseudo-di- and tetraacetylenic materials (**III**−**V**), some of the aromatic modes of the phenylene ring are also enhanced, in particular, the quadrant stretch at ~1600 cm^{-1} and the β_{C-H} band at 1175 cm^{-1}. Both of these vibrations have strong components along the direction of conjugation. The 1220 cm^{-1} band in **III** and **IV,** matched by a band at 1296 cm^{-1} in compound **V,** is identified by its substituent sensitivity as the ring C−C stretching mode, which includes a strong substituent stretching component. It is also considerably enhanced, although not as much, as the substituent motion is directly along the backbone chain and the other motions involved are also generally in this direction.

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Small intensity enhancements of the quadrant in-plane deformation bands at ~800 cm^{-1} for compounds **III** and **IV**, which include a component of substituent stretching motion in the *para*-disubstituted benzenes, are also evident. The other component of this vibration is mildly enhanced and appears at ~650 cm^{-1}. A deformation of the aromatic ipso carbon−acetylenic linkage is associated with a band at ~530 cm^{-1}, where it is difficult to identify in the presence of the Pt−C stretching band located at ~490 cm^{-1}. The behavior of these bands under the influence of high external pressures facilitates their assignment.[35]

The above bands are either missing or greatly shifted in the pseudo-tetraacetylenic material (**V**). The latter compound also exhibits a very strong fluorescence background, and thus, bands in this region may have been obscured. The substituent stretching motion in this compound is along the backbone direction, but the other components of the vibration are perpendicular to the framework of the polymer. Other modes with components perpendicular to the backbone, such as those primarily due to the aromatic C−H stretching motions, are not enhanced. A weak band appears in the Raman spectra of **I** and **V** at 971 and 988 cm^{-1}, respectively. This band remains unassigned but may relate to an even-numbered C≡CC≡C moiety. The bands at 1022 and 423 cm^{-1} do not have counterparts in the spectra of any of the other compounds, emphasizing the significant differences between **V** and the other polymers. The excitation of the electronic bands in this compound may cause structural changes in the backbone. Since the IR spectrum is not significantly different from those of **III** and **IV**, this would appear to be likely. Finally, the vibrations due to the tertiary phosphine and arsine ligands are extremely weak and are barely detectable in the presence of the backbone bands.

Also relevant to the electronic structure of these compounds is the fluorescence background seen in the Raman spectra. In the absence of direct fluorescence measurements, it is difficult to derive any conclusive evidence; however, there are differences in both the intensity and the position of the fluorescence bands. While there is no direct relationship between the amount of fluorescence and the resonance enhancement of the vibrational bands, there appears to be some relationship of the latter to the number of acetylene moieties in the repeat unit. The fluorescence is slightly less intense in the diacetylenic compound than in the triacetylenic one (see Figure 3, where a small rise in the baseline is observed) and very much so in the pseudo-diacetylenic compound compared with the pseudo-tetraacetylenic one. In the pseudo-tetraacetylenic compound, the intensity is significantly higher than in the other materials. In fact, this is the only compound where this fluorescence can be seen easily when the scale is normalized to the height of the C−H stretching vibrations (Figure 3). For the other compounds, the intensity of the fluorescence is small compared with that of the vibrations superimposed upon it. Moreover, the intensity of this band is less in the "pure" acetylenics than in the equivalent pseudo-acetylenic materials. Unlike the vibrational spectra, the fluorescence is dependent on the ancillary ligand, with the tertiary arsine-containing compound (**IV**) having a considerably reduced fluorescence compared with that for the analogous phosphine compound (**III**). It is possible that the metal orbitals involved in bonding with the ancillary ligands may also contribute to the metal acetylenic overlap. Although the fluorescence band is broad, the peak maximum does appear to shift from compound to compound but in a fashion which is difficult to interpret on the basis of these data.

The C≡C stretching vibrations observed in the Raman spectra are also consistent with the symmetry argument presented above. Both the number and positions of the bands are in accord with this proposal. Frequency differences between the IR and Raman bands are clearest in the polyacetylenic compounds (**I**, **II**), where differences of more than 40 cm^{-1} confirm the mutual exclusivity rule. The differences are less pronounced (5−10 cm^{-1}) in the compounds containing phenyldiethynyl (**III** and **IV**) and phenyldibutynyl (**V**) linkages but are consistent with a centrosymmetric group. As noted earlier, the diacetylenic compound is slightly anomalous in the IR. The Raman $\nu_{C\equiv C}$ band has an intensity and position consistent with those of the other compounds. However, this peak exhibits a shoulder at 2110 cm^{-1}, which may be the result of Fermi resonance interactions common in acetylenic materials,[8] since there are many overtone and combination bands near this peak. A breakdown in the symmetry argument cannot, however, be excluded. Clearly, a comparison of the di-, tri-, and tetraacetylenic subunits is not satisfactory. Although of the same symmetry, the vibrations give rise to bands that are different in detail from one chain length to another. In fact, the triacetylenic compound has a Raman $\nu_{C\equiv C}$ band at a position which is considered anomalous compared with the IR spectrum of a diacetylenic species. This frequency is therefore not anomalous for a vibration of these chains, and the two species have bands at very similar positions but reversed in activity.

The average value of the vibrational frequencies may be a more helpful measure of the factors influencing the bonding in these rigid-rod polymers. This is certainly the case for the di- (**I**, 2071 cm^{-1}), tri- (**II**, 2078 cm^{-1}), and pseudo-di- (**III**, 2103 cm^{-1}; **IV**, 2101 cm^{-1}) acetylenic polymers. The data for the pseudo-tetraacetylenic compound (**V**, 2120 cm^{-1}) are perhaps less informative. This information would imply that conjugation is greater (i.e., C≡C bond strength is less) for the "pure" acetylenics (**I** and **II**) than for those interrupted by phenylene rings (**III**−**V**). Any change in π-conjugation should also be reflected (and reversed) in the Pt−C stretching frequencies, as these bonds are the beneficiaries of the transfer of electron density out of the acetylene π-orbitals. This situation also applies to the first four com-

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pounds, with **I** and **II** having similar frequencies, which are higher than are those for **III** and **IV** (also similar to each other, Table 1). Compound **V** is different in this respect, having a value slightly higher than are those in the other species. This situation is also true of all the phenyl group vibrations in this compound compared with other phenyl-substituted materials. The phenyl group vibrations are all present, indicating a phenyl structure rather than a quinoidal analogue. The reasons for this are not clear. Theoretical and photoelectron studies[36−40] have shown that the conjugative interactions are of the filled−filled type, with Pt-π* back-bonding being of minimal importance. The result with respect to bond strengthening or weakening is the same regardless of the form.

The mutual exclusivity rule also appears to apply to the phenylene group vibrations. This is common for symmetrically *para*-di-substituted phenyl rings.[8] Raman bands are mostly absent from the corresponding IR spectra save apparently for the formally IR-forbidden 1600 cm^{-1} quadrant stretch mode. This region of the IR spectra is quite cluttered and the band is weak in the IR and strong in the Raman. It is possible that this IR band is due to either an overtone or a combination band. There are strong characteristic bands around 840 cm^{-1} in both the IR and Raman, but it is more likely that they arise from different vibrational motions. The IR-active band is most probably the strong out-of-plane phenyl ring deformation mode, and the Raman band is the substituent-sensitive a_g quadrant in-plane stretching vibration; these vibrations occur at similar frequencies by coincidence. These frequencies for the pseudo-tetraacetylenic polymer (**V**) are always higher than are those for other related species, perhaps reflecting the electron-rich nature of this material.

The ancillary ligand vibrations are weak in the Raman, showing none of the enhanced intensity of the rigid backbone groups. It is therefore difficult to compare these bands with the more prominent IR bands arising from the same groups. In general, the bands due to these ancillary groups do not vary significantly from compound to compound in either the IR or the Raman.

Conclusions

The vibrational spectra of polymeric *n*-acetylenic and pseudo-*n*-acteylenic bridged platinum(II) species are consistent with centrosymmetric rigid-rod forms, probably of C_{2h} or D_{2h} local symmetry. Despite considerable evidence of π-conjugation through the platinum atoms and along the acetylenic and pseudo-acetylenic chains, the backbone units are still essentially alternating acetylenic in character. Unlike purely organic chains, which are often more easily characterized as allene-like in nature, these conjugated chains are sufficiently broken at both the metal and, if present, at the aromatic rings to retain the electron density primarily between alternate carbon pairs. Clearly, π-conjugation is reduced by insertion of the phenylene rings into the backbone. This no doubt reflects the energy differences between the acetylenic and phenylene ring orbitals and may also relate to the disposition of the phenylene ring π-orbitals with respect to the platinum−acetylenic conjugated chain orbitals. Decreases in conjugation are seen as increases in the frequencies of acetylenic stretching vibrations between “pure” acetylenics and the pseudo-acetylenic polymers. Addition of acetylene moieties to pseudo-acetylenic materials (e.g., compound **V**) emphasizes the break at the aromatic ring, where metal π-interactions are delocalized over a longer chain fragment. This situation is reflected in an increase in the Pt−C stretching frequency despite an increase in the C≡C stretching frequency. Bonding within the aromatic ring also strengthens in this example, producing a concurrent increase in the phenylene frequencies. Breaking the conjugation with the phenylene ring increases the bond strength around the ring by reducing electron sharing with the acetylene π-system. Concurrently, the electron density along the chain is increased, increasing the C≡C stretching frequency. This high density would allow more interaction with the metal, thus increasing the Pt−C stretching frequency without reducing the overall carbon−carbon bond strength, relative to the other compounds. It is possible that ring rotation may accompany such a decrease in electron sharing, making the backbone less stereochemically rigid.

Vibrations in these rigid-rod compounds are strongly coupled to the electronic transitions of the delocalized backbone. This results in resonance enhancement of those vibrations lying along the direction of the backbone relative to those which are perpendicular to the backbone. Such enhancement upon near-IR irradiation demonstrates that the electronic bands of these materials extend significantly into the near-IR region of the spectrum. Variations in the fluorescence frequency and intensity reflect subtle changes in the electronic levels and, unlike the vibrational modes, are dependent on the nature of the ancillary ligand. In conclusion, vibrational spectroscopy can help delineate structural properties of conjugated acetylenic polymers which are important to their function as electronic materials.

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