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Synthesis and Structures of Extended-Chain Metal-Alkylidyne Compounds: Conjugated Polymers Composed of Alternating Organic and Transition-Metal Subunits

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Conjugated organic polymers are the subjects of intensive research because their bonding and physical properties are of fundamental interest and technological importance.[1] In principle, the substitution of unsaturated transition-metal centers for carbon within the conjugated backbones of these polymers should provide materials with significant structural and electronic tunability and, hence, enhanced properties. While many metal-containing organic polymers have been reported,[2] none of these possess the classic alternate-bond-order structure associated with conjugated organic polymers. Herein we report the syntheses and molecular structures of a class of conjugated, alternate-bond-order organometallic polymers. These species are noteworthy not only because they are the first examples of such polymers but because they exhibit broad structural flexibility and unusual photophysical properties as well.

We have reported[3] that the one-dimensional polyacetylene analogues[4] $[M(\equiv N)(OR)_3]_\infty$ (M = Mo, W)[5] are optical frequency-doubling materials and possess extremely long-lived electronic excited states. A new, broader class of polymers derived from these archetypes would result from substitution of the bridging nitrido ligand with the isoelectronic alkylidyne ligand, CR, where R is a conjugated organic moiety that is also capable of acting as a ligand and is thus able to promote self-assembly of $[-M\equiv CR-]_n$ polymers. Triple-bond metathesis[6] provides a synthetic route to such materials.

The reactions of the alkynylpyridines NC_5H_2-3,5-Me_2-4-$C\equiv CPr^n$ and NC_5H_4-3-$C\equiv CBu^n$ with either $W(CEt)(OBu^t)_3$[7] or $W_2(OBu^t)_6$[8] in benzene result in the formation of sparingly soluble yellow to orange precipitates. These compounds possess empirical formulas of $[W(\equiv C(4\text{-}NC_5H_2Me_2))(OBu^t)_3]$ (**1**) and $[W(\equiv C(3\text{-}NC_5H_4))(OBu^t)_3]$ (**2**), respectively, on the basis of elemental analyses, mass-spectral data, and ^{13}C-NMR spectroscopy.[9] The low solubility of these materials suggests that they are polymeric; by comparison, monomeric $M(CR)(OR')_3$ ($R \neq$ pyridyl (pyr)) complexes are readily soluble in nonpolar organic solvents.[7]

Single-crystal X-ray diffraction studies[10] of **1** and **2** confirmed that both compounds are polymeric in the solid state (Figures 1 and 2), consisting of roughly planar, zigzag arrays of $W(C\text{-}pyr)(OBu^t)_3$ units connected by W-N bonds in a head-to-tail fashion. The asymmetric unit of each crystal contains two $[W(C\text{-}pyr)(OBu^t)_3]$ building blocks. For $[\mathbf{1}]_\infty$, these crystallographically distinct monomers (**A** and **B**) are bonded to each other, such that all polymer chains repeat in an **A**–**B**–**A**–**B** fashion, while crystals of $[\mathbf{2}]_\infty$ consist of two different chains, one of which is exclusively composed of **A** repeat units, and the other of which is solely **B**. The short W≡C bond distances for both $[\mathbf{1}]_\infty$ (1.766(13), 1.770(15) Å) and $[\mathbf{2}]_\infty$ (1.775(9), 1.789(8) Å) and the W—O bond distances ($[\mathbf{1}]_\infty$, 1.907[9] Å; $[\mathbf{2}]_\infty$, 1.883[6] Å) are similar to those of the related monomer $W(CPh)(OBu^t)_3$ ($d(W\equiv C)$ = 1.758(5) Å, $d(W\text{-}O)_{av}$ = 1.865[4] Å).[11]

A conspicuous difference between the two polymers is that the tungsten geometry in $[\mathbf{1}]_\infty$ is pseudo square pyramidal, with the alkylidyne ligand occupying the apical position ($\angle C\equiv W-N$ = 95.6(5), 97.5(5)°), while that in $[\mathbf{2}]_\infty$ is pseudo trigonal bipyramidal, with equatorial alkoxide ligands and a trans C≡W—N linkage ($\angle C\equiv W-N$ = 173.6(4), 174.6(3)°) (Figure 2). An immediate consequence of this difference in structure is that the W-N bond distances of $[\mathbf{1}]_\infty$ (2.253(12), 2.273(10) Å), which are within the expected ranges for tungsten-pyridine complexes,[12] are decidedly shorter than those for $[\mathbf{2}]_\infty$ (2.523(7), 2.534(7) Å), with the longer distances of the latter arising from the strong trans influence of the alkylidyne ligand.

The observation of both limiting pentacoordination geometries for these polymers is striking, in view of their similar compositions. On the basis of the stronger W-N bonding in $[\mathbf{1}]_\infty$, the square-pyramidal structure would appear to be electronically preferred, although it is well established that the potential-energy surface that connects the square-pyramidal and trigonal-bipyramidal limits is characterized by relatively shallow minima.[13] Given this, and the electronic similarity of the 3-pyridyl and 4-lutidyl alkylidyne R groups, it seems likely that differences among the intra- and interchain steric interactions are responsible for the differing structures of $[\mathbf{1}]_\infty$ and $[\mathbf{2}]_\infty$. These steric differences appear to be traceable to meta versus para substitution of the heterocycle. Specifically, the torsional freedom of the lutidyl group of $[\mathbf{1}]_\infty$ enables the sterically constrained cis coordination of lutidyl and alkylidyne ligands via twisting of the lutidyl ring out of the C≡W—N plane of the polymer (Figure 1a). In contrast, the adoption of a square-pyramidal geometry by $[\mathbf{2}]_\infty$ would be accompanied either by severe ring–ring repulsions, in the limit of a planar polymer, or by buckling of the polymer backbone. A space-filling model of $[\mathbf{1}]_\infty$ indicates that the lutidyl rings are as close as possible to being coplanar with the polymer backbone without being in a sterically unfavorable position; the torsion angles (as defined relative to the C≡W—N plane) for the two rings in the asymmetric unit are ca. 10 and 40°.

The structural data for $[\mathbf{1}]_\infty$ and $[\mathbf{2}]_\infty$ indicate that the bonding of both polymers can be described by limiting valence-bond

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[9] Analytical and spectroscopic data for **1** and **2** are available as supplementary material.

[10] Crystals of $[\mathbf{1}]_\infty$ and $[2\cdot(^1/_2C_6H_6)]_\infty$ were obtained directly from the reaction mixture. $[\mathbf{1}]_\infty$: $Pna2_1$, a = 25.981(3) Å, b = 15.333(2) Å, c = 11.725(2) Å, V = 4670.9(9) Å^3, Z = 8, d_{calcd} = 1.483 g cm^{-3}, μ = 49.62 cm^{-1}, T = 228 K, 4.0° ≤ 2θ ≤ 48.0°, independent reflections = 7318, observed reflections = 5848 ($F > 6\sigma(F)$), absorption correction by XABS, R_F = 3.74%, R_{wF} = 4.78%. $[2\cdot(^1/_2C_6H_6)]_\infty$: $P2_1/n$, a = 17.408(3) Å, b = 14.422(3) Å, c = 19.965(5) Å, β = 107.20(2)°, V = 4788(2) Å^3, Z = 8, d_{calcd} = 1.477 g cm^{-3}, μ = 48.42 cm^{-1}, T = 294 K, 4.0° ≤ 2θ ≤ 50.0°, independent reflections = 8434, observed reflections 4196 ($F > 5\sigma(F)$), absorption correction by XEMP, R_F = 2.75%, R_{wF} = 2.54%.

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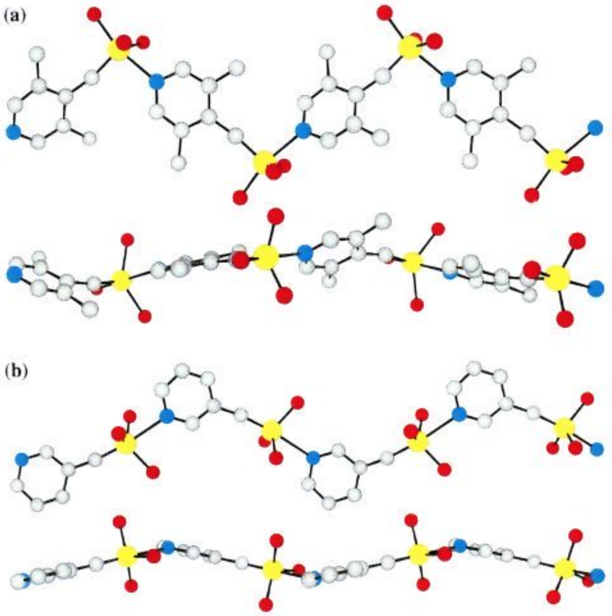


Figure 1. Face and edge views of tetrameric sections of (a) $[\mathbf{1}]_\infty$ and (b) the **A** strand of $[\mathbf{2}\cdot(^1/_2C_6H_6)]_\infty$. Atoms are color coded as follows: W, yellow; N, blue; O, red; C, gray. Hydrogen atoms, *tert*-butyl groups, and interstitial C_6H_6 molecules have been omitted for clarity.

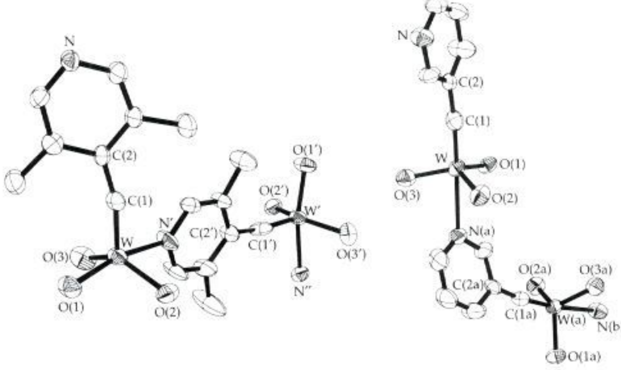
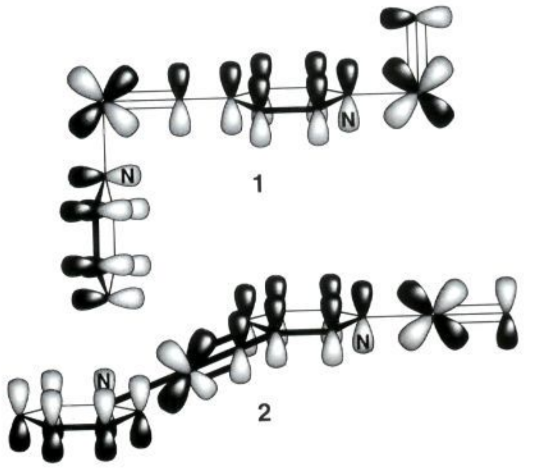


Figure 2. Structural skeletons of the asymmetric unit of $[\mathbf{1}]_\infty$ (left) and an **A–A** unit of $[\mathbf{2}\cdot(^1/_2C_6H_6)]_\infty$ (right); an additional nitrogen atom is shown ligated to the tungsten terminus of each dimer. Nuclei are represented by thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and bond angles (deg) for $[\mathbf{1}]_\infty$ are as follows: W–C(1) = 1.766(13), 1.770(15); W–N′ = 2.253(12), 2.273(10); W–O(1) = 1.940(10), 1.913(10); W–O(2) = 1.911(9), 1.897(8); W–O(3) = 1.886(9), 1.895(8); W–C(1)–C(2) = 165.8(10), 172.1(12); C(1)–W–N′ = 95.6(5), 97.5(5); C(1)–W–O(1) = 98.8(5), 97.0(6); C(1)–W–O(2) = 112.9(5), 108.4(6); C(1)–W–O(3) = 110.0(5), 110.9(6). Selected bond distances (Å) and bond angles (deg) for the **A** and **B** strands of $[\mathbf{2}]_\infty$ are as follows: W–C(1) = 1.775(9), 1.789(8); W–N(a) = 2.523(7), 2.534(7); W–O(1) = 1.887(6), 1.882(6); W–O(2) = 1.874(6), 1.888(5); W–O(3) = 1.879(6), 1.889(6); W–C(1)–C(2) = 172.5(8), 177.6(8); C(1)–W–N(a) = 173.6(4), 174.6(3); C(1)–W–O(1) = 104.2(4), 101.6(3); C(1)–W–O(2) = 102.9(3), 104.0(3); C(1)–W–O(3) = 101.9(3), 104.8(4).

canonical structures in which the bond order alternates along the backbone. In view of this, an obvious question is whether these polymers are π-conjugated. From the standpoint of the π-orbital overlap between the W≡C and heterocyclic fragments, the structural difference between $[\mathbf{1}]_\infty$ and $[\mathbf{2}]_\infty$ has important consequences. For $[\mathbf{1}]_\infty$, the orientation that provides maximum π-overlap is that in which the rings are perpendicular to the C≡W—N backbone, while for $[\mathbf{2}]_\infty$ the corresponding structure is planar. Although the structure observed for $[\mathbf{2}]_\infty$ is nearly optimum in this regard, the ring torsion angles for $[\mathbf{1}]_\infty$ limit π-overlap (in the solid state) to ca. 10% of the maximum value. Nonetheless, a continuous π-orbital pathway along the backbone is allowed by symmetry for both polymers.



A remarkable property of these polymers that seems likely to be connected to their unusual bonding and structures is that they are luminescent at room temperature in both the solid state and fluid solution (λ_{max} (solid state, 77 K) for $[\mathbf{1}]_\infty$, 635 nm; for $[\mathbf{2}]_\infty$, 640 nm). This is surprising both because monomeric W(CR)(OBu^t)$_3$ (R = alkyl, aryl) complexes fail to luminesce under comparable conditions and because solution-phase emission from LMCT states is extremely rare.[14] The emission spectrum of $[\mathbf{1}]_\infty$ at ca. 20 K displays vibronic structure consisting of four resolved features spaced at ca. 1000 cm^{-1} intervals, of which the 0–1 transition is most intense. Although the vibrational spectra of these polymers are too complex to straightforwardly interpret, the only reasonable assignment for this frequency is to modes associated with the $[\text{W≡C—pyr}]_\infty$ backbone, since it is comparable to the frequencies of ν(W≡C)[15] and of several lutidyl modes,[16] whereas modes involving the W—O and W—N coordinates should not have frequencies above ca. 600 and 400 cm^{-1}, respectively.[17] The intensity profile of this vibronic progression suggests that the [W≡C—pyr] π system contributes significantly to the frontier orbitals of these polymers. A preliminary observation consistent with the presence of extended π-interactions in $[\mathbf{1}]_\infty$ and $[\mathbf{2}]_\infty$ is that the onsets of their emission bands are red shifted ca. 2600 and 2300 cm^{-1}, respectively, from that of W(CPh)(OBu^t)$_3$ (T = 25 K).

We believe these mixed organic–inorganic polymers to be prototypes of a broad new class of structurally and electronically flexible materials. The physical properties and fundamental structure/bonding relationships that characterize these polymers are under investigation.

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Supplementary Material Available: Listings of analytical, mass-spectral, and ^{13}C-NMR data and positional and thermal parameters for **1** and **2** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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