One-dimensional alignment of organometallic donor–acceptor compounds *via* coordination polymerization. Synthesis and structures of $[W(\equiv CC_6H_4X\text{-}4)(OBu^t)_3]_\infty$ (X = NMe_2, SMe)

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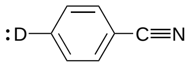
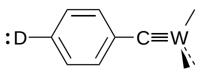
Metal–alkylidyne complexes of the type $W(\equiv CC_6H_4X\text{-}4)(OBu^t)_3$ (X = NMe_2, SMe), which are analogues of classic organic donor–acceptor compounds, form infinite-chain structures in the solid state through weak intermolecular dative bonds between the tungsten and donor atoms.

A design prerequisite for bulk molecular materials that possess second-order non-linear optical responses is that the individual chromophores of which they are composed must be non-centrosymmetrically ordered. One strategy for achieving this order is to incorporate the chromophore, typically a conjugated organic molecule with electron-donor (D) and -acceptor (A) substituents, into a polymer host, upon which the host–guest material is processed to induce temporary alignment of the chromophore dipoles, or *via* chemical bonds into a lattice of appropriate three-dimensional structure.[1] A second approach is to design chromophores that 'self-assemble' into ordered arrays, such as hydrogen-bonded networks of organic compounds[2] or metal coordination polymers.[3]

Our interest in developing transition-metal analogues of conjugated organic compounds and polymers[4] led us to inquire if replacing the ubiquitous cyano groups of organic donor–acceptor compounds **A** with metal–alkylidyne groups **B** would serve the dual purposes of broadening the electronic tunability of the acceptor and of affecting one-dimensional A–D···A–D ordering of the chromophores. Alkylidyne complexes of the type $M(\equiv CR)X_3$ (M = Mo, W)[5] are especially interesting in this context because the metal centres are potential electron acceptors (formally M^{VI}), and because they weakly coordinate neutral ligands *trans* to the M≡C bond, which can lead to one-dimensional polymeric structures if the alkylidyne R group contains a ligating substituent.[6] Herein we report the syntheses of $W(\equiv CC_6H_4NMe_2\text{-}4)(OBu^t)_3$ **1** and $W(\equiv CC_6H_4SMe\text{-}4)(OBu^t)_3$ **2**, and that these complexes exhibit one-dimensional A–D···A–D polymeric structures in the solid state.



A



B

Compounds **1** and **2** can be prepared from the reaction between $4\text{-}XC_6H_4CN$ (X = NMe_2, SMe) and $W_2(OBu^t)_6$[7] in pentane at room temp. Within minutes of combining the reagents the reaction mixture changes from deep red to brown, and white $[WN(OBu^t)_3]_\infty$[8] precipitates. Filtration of the solution and removal of solvent *in vacuo* yields a brown powder. Recrystallization of this material from pentane at −35 °C provides yellow–orange **1** and **2** in 73 and 74% yield (based on $4\text{-}XC_6H_4CN$), respectively.† The ^1H and ^{13}C NMR data for **1** and **2** are similar to those for the related compound $W(\equiv CPh)(OBu^t)_3$.[9] There is no evidence from the NMR data for static intermolecular interactions among monomers in solution.

Single-crystal X-ray diffraction studies of **1** and **2** reveal them to be polymeric in the solid state, consisting of one-dimensional zigzag chains of monomers connected by weak dative bonds between the donor and tungsten atoms of adjacent molecules.‡ The structures of the repeat units of $[\mathbf{1}]_\infty$ and $[\mathbf{2}]_\infty$ are shown in Fig. 1, and a view of an extended fragment of $[\mathbf{1}]_\infty$ is provided in Fig. 2. The assembly of **1** and **2** into infinite-chain structures does not result in significant structural perturbations to their WCO_3 cores: the W≡C bond distances of $[\mathbf{1}]_\infty$ [1.754(7) Å] and $[\mathbf{2}]_\infty$ [1.757(6) Å] are essentially identical to that of $W(\equiv CPh)(OBu^t)_3$ [1.758(5) Å],[10] and there is only a slight flattening of the pyramidal WO_3 units of $[\mathbf{1}]_\infty$ and $[\mathbf{2}]_\infty$ as a result of the axial ligation in the polymers [$O\text{–}W\text{–}O_{av}$: $[\mathbf{1}]_\infty$ 115(1)°, $[\mathbf{2}]_\infty$ 114(2)°, $W(\equiv CPh)(OBu^t)_3$ 111(2)°]. From an electronic standpoint, only small structural perturbations are expected because the intermolecular W···E bonds in $[\mathbf{1}]_\infty$ and $[\mathbf{2}]_\infty$ are extremely long [W···N 2.767(4), W···S 3.079(2) Å]. Steric interactions and packing forces are presumably responsible for the more noticeable distortions, such as the slight 'bowing' of the $E\text{–}C_6H_4\text{–}C\equiv W$ unit (Fig. 2).

Despite the long W···N bond distance, the electronic structure of the aniline moiety in $[\mathbf{1}]_\infty$ is significantly altered from that expected for monomeric **1**. Specifically, the nitrogen centres in $[\mathbf{1}]_\infty$ are pyramidal [C(5)–N–C(6) 113.9(3)°, C(6)–N–C(6a) 110.9(6)°], in contrast to the expected planar structure, and the C(5)–N bond distance [1.438(8) Å] is consistent with sp^3 hybridization for nitrogen rather than sp^2 hybridization [$d(C_{aryl}\text{–}N_{sp^3})$ = 1.43 Å, $d(C_{aryl}\text{–}N_{sp^2})$ = 1.37 Å].[11] This

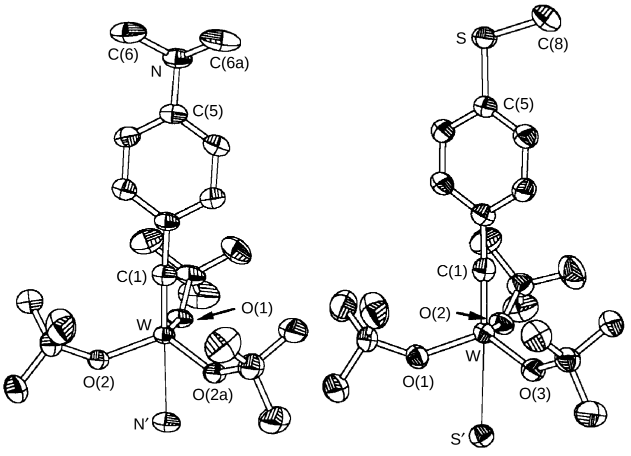


Fig. 1 Thermal ellipsoid representations (50% probability) of the structures of **1** (left) and **2** (right). The donor atoms of the adjacent molecules are also shown. Selected bond distances (Å) and bond angles (°): for **1**: W–C(1) 1.754(7), W···N 2.767(4), W–O(1) 1.868(4), W–O(2) 1.876(3), C(5)–N 1.438(8); C(5′)–N′–W 107.5(4), N′–W–C(1) 174.2(3), O(1)–W–O(2) 115.2(1), O(2)–W–O(2a) 113.2(2), C(1)–W–O(1) 101.4(3), C(1)–W–O(2) 104.9(1), W–C(1)–C(2) 170.8(5), C(5)–N–C(6) 113.9(3), C(6)–N–C(6a) 110.9(6); for **2**: W–C(1) 1.757(6), W···S 3.079(2), W–O(1) 1.873(4), W–O(2) 1.881(4), W–O(3) 1.894(4), C(5)–S 1.772(5); C(5′)–S′–W 101.9(2), S′–W–C(1) 173.6(2), O(1)–W–O(2) 115.3(2), O(1)–W–O(3) 111.4(2), O(2)–W–O(3) 115.3(2), W–C(1)–C(2) 174.0(4), C(5)–S–C(8) 103.9(3).

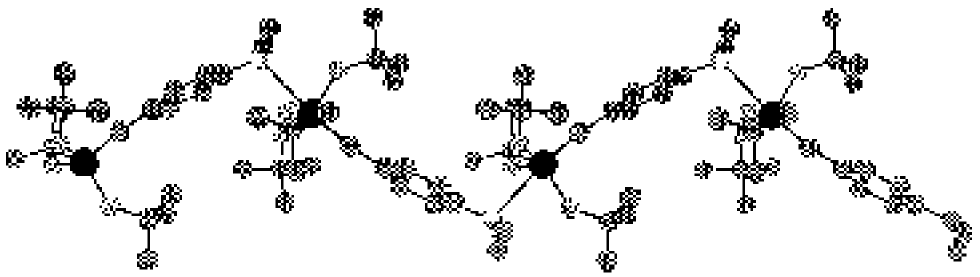
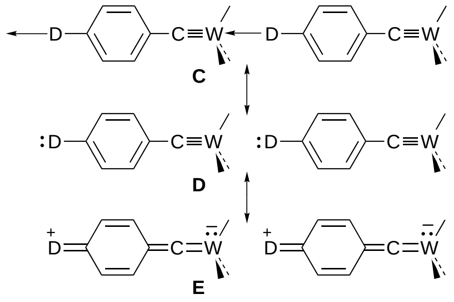


Fig. 2 Tetrameric section of [W(≡$CC_6H_4NMe_2$-4)(OBu^t)$_3$]$_\infty$. Atoms are shaded as follows: tungsten, black; oxygen, dotted; carbon, grey; nitrogen, hatched.

indicates that the π interaction between the NMe_2 and aryl groups is significantly diminished from what it would be in the monomeric compound. For [**2**]$_\infty$, in contrast, the C(5)–S bond distance [1.772(5) Å] is typical of that for an organic thioanisol [d(C_{aryl}–S) = 1.77 Å],[11] suggesting that the S–aryl π-interactions are of comparable magnitude in both the polymer and monomer forms. In principle, strong D $\longrightarrow$ {C≡W(OBu^t)$_3$} interactions should be manifested as a quinoidal distortion of the aryl rings, but the C–C distances {[**1**]$_\infty$ 1.378(6)–1.386(6) Å, [**2**]$_\infty$ 1.369(8)–1.411(8) Å} are not known with sufficient precision to draw any conclusions on this point. We are presently studying the electronic spectra of these materials to deduce the extent of their D $\longrightarrow$ {C≡W(OBu^t)$_3$} charge transfer.

In summary, we have discovered a class of organometallic analogues of classic organic *para*-phenylene D–A compounds that form one-dimensional solid-state structures. Qualitatively describing the bonding in these polymers requires the use of a third valence-bond canonical structure (**C**) in addition to the two typically invoked for monomeric D–A compounds (**D**, **E**).



From the standpoint of designing non-linear optical materials, achieving the optimum balance among these structures through chemical modifications involves trade offs; attempting to favour intramolecular D $\longrightarrow$ A charge transfer (**E**) by increasing the electron-withdrawing capacity of the metal (*e.g.* the use of less strongly donating ancillary ligands) will also strengthen, detrimentally, the intermolecular interactions (**C**). Fortunately, the extremely long W···E bond distances in [**1**]$_\infty$ and [**2**]$_\infty$ suggest that even a very weak dative interaction is sufficient to affect one-dimensional organization of this class of compounds, and thus that steric modification of the ancillary ligands or of the donor group may allow independent tuning of intra- and inter-molecular charge transfer. Experiments to test this hypothesis are in progress. An additional challenge is to engineer non-centrosymmetric space groups for these materials, as those for **1** and **2** are centrosymmetric; derivatives with chiral ancillary ligands should be important in this context.

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Footnotes

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† For **1**: ^{1}H NMR (C_6D_6): δ 7.34 (d, 2 H, C_6H_4), 6.60 (d, 2 H, C_6H_4), 2.54 [s, 6 H, N(CH_3)$_2$], 1.56 [s, 27 H, OC(CH_3)$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): δ 258.5 (s with satellites $^1J_{CW}$ 309.4 Hz, W≡C), 149.3 (s, C_6H_4), 139.3 (s, C_6H_4), 133.6 (s, C_6H_4), 112.2 (s, C_6H_4), 81.1 [s, O*C*(CH_3)$_3$], 40.6 [s, N(CH_3)$_2$], 33.1 [s, OC(*C*H_3)$_3$]. For **2**: ^{1}H NMR (C_6D_6): δ 7.22 (d, 2 H, C_6H_4), 2.00 [s, 3 H, S(CH_3)], 1.49 [s, 27 H, OC(CH_3)$_3$]; the second C_6H_4 resonance was obscured by the solvent. ^{13}C{^{1}H} NMR (C_6D_6): δ 257.3 (s with satellites $^1J_{CW}$ 305.2 Hz, W≡C), 145.8 (s, C_6H_4), 136.6 (s, C_6H_4), 133.1 (s, C_6H_4), 126.5 (s, C_6H_4), 81.5 [s, O*C*(CH_3)$_3$], 33.0 [s, OC(*C*H_3)$_3$], 16.2 [s, S(CH_3)].

‡ *Crystal data*: for **1**: $C_{21}H_{37}NO_3W$, M = 535.37, orthorhombic, space group $Pnma$, a = 16.389(11), b = 15.529(9), c = 9.336(6) Å, V = 2376(3) Å^3, Z = 4, D_c = 1.497 g cm^{-3}, F(000) = 1072. 2827 independent reflections were collected and used in structure solution and subsequent least-squares refinement on F^2. $R1$ = 0.0515 (all data), $wR2$ = 0.0780 (all data), GOF = 1.023. For **2**: $C_{20}H_{34}O_3SW$, M = 538.38, monoclinic, space group $P2_1/n$, a = 8.527(1), b = 16.409(3), c = 16.746(3) Å, β = 97.11(3)°, V = 2325.1(7) Å^3, Z = 4, D_c = 1.538 g cm^{-3}, F(000) = 1072. Of 5677 reflections collected, 5326 independent reflections were used in structure solution and subsequent least-squares refinement on F^2. $R1$ = 0.0521 (all data), $wR2$ = 0.0987 (all data), GOF = 1.024. Data for both crystals were collected at −65 °C with Mo-Kα radiation and were corrected for absorption. Direct-method solutions yielded positions of all non-hydrogen atoms, which were refined anisotropically. Hydrogen-atom positions were calculated [d(C–H) = 0.96 Å]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/453.

References

1 *Polymers for Second-Order Nonlinear Optics*, ed. G. A. Lindsay and K. D. Singer, American Chemical Society, Washington, DC, 1995; T. J. Marks and M. A. Ratner, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 155; L. R. Dalton, A. W. Harper, R. Ghosn, W. H. Steier, M. Ziari, H. Fetterman, Y. Shi, R. V. Mustacich, A. K.-Y. Jen and K. J. Shea, *Chem. Mater.*, 1995, **7**, 1060.

2 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311; J. C. MacDonald and G. M. Whitesides, *Chem. Rev.*, 1994, **94**, 2383.

3 C.-T. Chen and K. S. Suslick, *Coord. Chem. Rev.*, 1993, **128**, 293.

4 T. P. Pollagi, J. Manna, S. J. Geib and M. D. Hopkins, *Inorg. Chim. Acta*, 1996, **243**, 177 and references therein.

5 J. S. Murdzek and R. R. Schrock, in *Carbyne Complexes*, ed. H. Fischer, P. Hofmann, F. R. Kreissl, R. R. Schrock, U. Schubert and K. Weiss, VCH, Weinheim, 1988, pp. 147.

6 T. P. Pollagi, S. J. Geib and M. D. Hopkins, *J. Am. Chem. Soc.*, 1994, **116**, 6051.

7 M. H. Chisholm, B. W. Eichhorn, K. Folting, J. C. Huffman, C. D. Ontiveros, W. E. Streib and W. G. Van Der Sluys, *Inorg. Chem.*, 1987, **26**, 3182.

8 R. R. Schrock, M. L. Listemann and L. G. Sturgeoff, *J. Am. Chem. Soc.*, 1982, **104**, 4291.

9 M. L. Listemann and R. R. Schrock, *Organometallics*, 1985, **4**, 74.

10 F. A. Cotton, W. Schwotzer and E. S. Shamshoum, *Organometallics*, 1984, **3**, 1770; *J. Organomet. Chem.*, 1985, **296**, 55.

11 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

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