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Thienyl carboxylate ligands bound to M_2 quadruple bonds involving molybdenum and tungsten. Models for dimetallated polythiophenes

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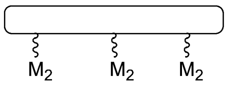
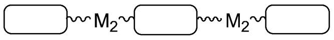
Thienyl-carboxylate and -dicarboxylate groups attached to dinuclear centers (M = Mo or W) having MM quadruple bonds show interesting electronic properties and provide insight into the probable nature of related dimetallated polythiophenes.

The incorporation of metal ions, particularly transition and lanthanide element ions into conjugated organic polymers[1] is attracting considerable attention as chemists address the challenges posed by synthesis and processing, and the way in which metal ions might be used to further enhance the potential applications of this class of polymers. Examples of well studied systems include metallocene derived polymers[2] and metallated poly-ynes,[3] polyphenylvinylenes[4] and polythiophenes.[5] We were attracted to the idea of incorporating M_2 units with MM quadruple bonds into conjugated polymers since these dinuclear units have interesting electrochemical and optical properties.[6] We describe here our synthesis and preliminary characterizations of some M_2^{4+}-thienylcarboxylate containing compounds of molybdenum and tungsten. These serve as model compounds for when the M_2 unit is either attached to the polymer as an electronically coupled appendage or is incorporated within the back-bone, as shown schematically in **A** and **B**, respectively.

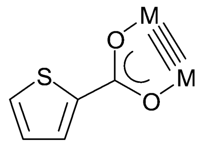


A

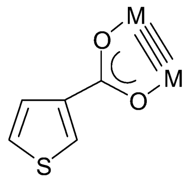


B

The frontier molecular orbitals of a MM quadruple bond are the M_2 σ, π and δ orbitals of which δ lie highest in energy and can interact strongly with the CO_2 π orbitals of a carboxylate. Thus, thienylcarboxylate ligands, $ThCO_2^-$, attached to the dinuclear unit may serve as models for the attachment or incorporation of the M_2 units within polythiophenes. Considerations of M_2 δ to ligand π bonding lead one to expect the strongest electronic coupling between the M_2 and Th centers to occur when the CO_2 moiety is attached at the 2 relative to the 3 position and for 2,5-thienyldicarboxylate relative to their 3,4-counterparts (see **C**, **D**, **E** and **F**). We have described this type of bonding in detail for oxalate bridge M_4 complexes.[7,8]

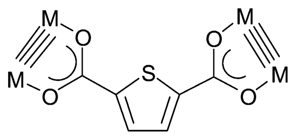


C [2-Th(CO_2)]

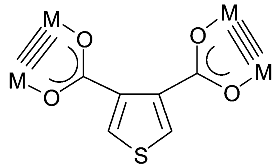


D [3-Th(CO_2)]

The reaction of $[M_2(O_2C^tBu)_4]$ (M = Mo[9], W[10]) and an equimolar amount of the respective thienylcarboxylic acids were performed in toluene and stirred for at least 5 d. The solids isolated from these reactions appear to be a mixture of the compounds $[M_2(O_2C^tBu)_{4-x}(O_2CTh)_x]$ ($x = 0 \rightarrow 4$) as detected by ^1H NMR spectroscopy and MALDI mass spectroscopy for



E [2,5-Th(CO_2)$_2$]



F [3,4-Th(CO_2)$_2$]

the molybdenum complexes. With these results, we decided to prepare the tetrakisthienylcarboxylate complexes compounds $[M_2(2\text{-}ThCO_2)_4]$ and $[M_2(3\text{-}ThCO_2)_4]$ (M = Mo, W).† These solids show intense absorptions in the visible region of the spectrum that arise from M_2 δ to thienylcarboxylate π* transitions.‡ As is shown in Fig. 1 these transitions are at lower energy than the M_2 δ to CO_2 π* transition of the parent compounds and substitution by 2-$ThCO_2$ produces a significant red shift in comparison to 3-$ThCO_2$. The spectra of the W_2-containing compounds are notably red-shifted in comparison to their molybdenum counterparts and the intensities of the absorptions are greater. This correlates well with the fact that the W_2 δ^2 electrons are roughly 0.5 eV higher in energy than their Mo_2 counterparts[6] and that the intensity of a fully allowed MLCT transition is proportional to the square of the overlap of the interacting orbitals.

The reaction of $[M_2(O_2C^tBu)_4]$ (M = Mo, W) with 2,5-thienyldicarboxylic acid gives either a red (M = Mo) or blue (M = W) precipitate from toluene which is consistent with the bridged complexes $[\{(M_2(O_2C^tBu)_3\}_2(2,5\text{-}Th(CO_2)_2)]$.† These thienyldicarboxylate complexes serve to further illustrate the aforementioned trends found for the thienylcarboxylate complexes. The electronic spectra of 2,5-thienylcarboxylates are strongly red-shifted as shown in Fig. 2. This is because the 2,5-carboxylate has a low lying π* orbital with extensive delocalization arising from the resonance form shown schematically in **G**.

As in oxalate bridged M_2 quadruply bonded complexes the HOMO and HOMO-1 orbitals are the out- and in-phase M_2 δ combinations that mix with the CO_2 π orbitals as shown in **H**

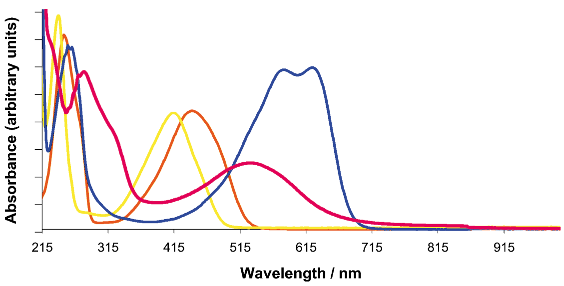


Fig. 1 Electronic absorption of the isolated solids $[Mo_2(2\text{-}Th(CO_2)_4)]$ (orange) (λ_{max}/nm (ε in $M^{-1}cm^{-1}$) = 441 (18,850) and 248 (30,900)), $[Mo_2(3\text{-}Th(CO_2))_4]$ (yellow) (415 (11,850) and 239 (21,750)), $[W_2(2\text{-}Th(CO_2)_4]$ (blue) (λ_{max}/nm (ε in $M^{-1}cm^{-1}$) = 624 (20,000), 583 (20,000) and 256 (31200)) and $[W_2(3\text{-}Th(CO_2)_4)]$† (red) ($\lambda_{max}$ / nm (ε in $M^{-1}cm^{-1}$) = 525 (2400), 328 (sh, 3550), 278 (5700) and 226 (sh, 7000) in THF solutions at room temperature.

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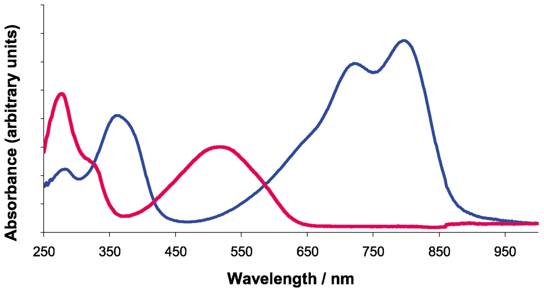
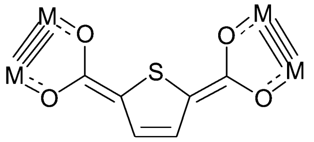
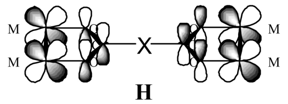


Fig. 2 Electronic absorbance of $[\{W_2(O_2C^tBu)_3\}_2(2,5\text{-}Th(CO_2)_2)]$ (blue) (λ_{max}/nm (ε in $M^{-1}cm^{-1}$) = 797 (35,900), 720 (31,500), 640 (16,100), 362 (21,450), 282 (11,100)) and $[\{Mo_2(O_2C^tBu)_3\}_2(2,5\text{-}Th(CO_2)_2)]$ (red) (λ_{max}/nm (ε in $M^{-1}cm^{-1}$) = 515 (16,000), 322 (sh, 13,050), 277 (26,600)) in THF solutions at room temperature.

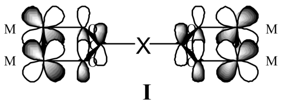


G

and **I**.[7,8] The back-bonding in **I** favours a planar bridged structure and leads to a stabilization of this orbital while the out-of-phase M_2 δ combination in **H** is destabilized as a result of the filled interactions. The importance of the back-bonding to the ligand bridge, as depicted by **H**, can be seen in the observation of a vibronic progression, associated with the thienylcarboxylate ligand, in the MLCT band of the W_4-containing complex as shown in Fig. 2.[7,8] No such orbital mixing is possible for the 3,4-thienyldicarboxylates.



H



I

Further evidence of the strong orbital mixing in the 2,5-thienyldicarboxylates can be seen in the EPR spectra of the radical cationic complexes prepared from the reactions of the neutral bridged complexes with $[Cp_2Fe][PF_6]$ in THF/CH_2Cl_2. In the case of tungsten the hyperfine spectra indicate electron delocalization over four metal atoms, g_{av} = 1.832, A_{avg} = 29.7 G (^{183}W, I = $^1/_2$, 14.3% natural abundance) but for molybdenum the odd electron is localized on one Mo_2 center *i.e.* is valence trapped on the EPR timescale g_{av} = 1.943, A_{avg} = 27.4 G (^{95}Mo, ^{97}Mo, I = $^5/_2$, 28% combined natural abundance).[12]

Polythiophenes are semiconductors with tuneable band gaps in the range 2.5 to 3.5 eV depending upon their substituents.[1] Given the results reported here and the ready functionalization of polythiophenes with carboxylate groups, we anticipate that the M_2 doped polymers should show interesting optical and electronic properties. For example, the W_2 δ electrons should lie higher in energy than the filled valence band and afford low energy photo-induced charge transfer into the polymer conduction band. Oxidation will occur preferentially at the W_2-center and depending upon the mode of W_2- attachment/incorporation we might anticipate interesting optical and electronic behaviour. Further studies along these lines are in progress.

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Notes and references

† **$[Mo_2(2\text{-}ThCO_2)_4]$**: $[Mo(CO)_6]$ (2.00 g, 7.58 mmol) and $2\text{-}ThCO_2H$ (2.91 g, 22.7 mmol) was refluxed for 16 h in a mixture of $1,2\text{-}C_6H_4Cl_2$ (100 mL) and THF (50 ml) under an argon atmosphere. An orange solid was filtered from the solution *via* a frit after allowing the solution to cool to room temperature. This solid (1.82 g, 94% yield) was washed twice with hexanes and then dried *in vacuo* for 4 h. Microanalysis: Found, C 34.34, H 1.69%. $C_{20}H_{12}O_8S_4Mo_2$ requires C 34.30, H 1.73%. NMR (THF-d_8): δ_H (400 MHz) 7.81 (4H, dd, J_{HH} = 3.7 and 1.3 Hz), 7.57 (4H, dd, J_{HH} = 5.0 and 1.3 Hz), 7.10 (4H, dd, J_{HH} = 5.0 and 3.7 Hz). MALDI-MS: 700 (100%, M^+). **$[W_2(2\text{-}ThCO_2)_4]$**: $[W_2(O_2C^tBu)_4]$ (119 mg, 0.154 mmol) was dissolved in toluene (*ca.* 15 ml) in a Schlenk flask and to this clear yellow solution $2\text{-}ThCO_2H$ (79 mg, 0.616 mmol) was added. The colour changed immediately to a deep purple and this solution was then stirred for 3 days at room temperature. 59 mg (43.7% yield) of this purple solid was filtered *via* a frit and washed with toluene then hexanes. Microanalysis: Found, C 25.70, H 1.87%. $C_{20}H_{12}O_8S_4W_2$ requires C 27.41, H 1.38%. NMR (THF-d_8): δ_H (400 MHz) 7.72 (4H, dd, J_{HH} = 3.7 and 1.3 Hz), 7.66 (4H, dd, J_{HH} = 5.0 and 1.3 Hz), 7.09 (4H, dd, J_{HH} = 5.0 and 3.7 Hz). **$[\{W_2(O_2C^tBu)_3\}_2(2,5\text{-}Th(CO_2)_2)]$**: The reaction was performed under similar conditions to that described for the preparation of $[W_2(2\text{-}ThCO_2)_4]$ using 600 mg of $[W_2(O_2C^tBu)_4]$ (0.777 mmol) and 65 mg of $2,5\text{-}Th(CO_2H)_2$ (0.378 mmol) The reaction was stirred at room temperature for 7–10 days. A deep blue solid (545 mg, 95% yield) was isolated by filtration *via* a frit. Microanalysis: Found, C 27.05; H 3.89%. $C_{36}H_{56}O_{16}SW_4$ requires C 28.59, H 3.73%. NMR (THF-d_8): δ_H (250 MHz) 7.28 (s, 2H, $2,5\text{-}C_4H_2S(CO_2)_2$); 1.40 (s, 18H, $O_2CC(CH_3)_3$); 1.36 (s, 36H, $O_2CC(CH_3)_3$). **$[\{Mo_2(O_2C^tBu)_3\}_2(2,5\text{-}Th(CO_2)_2)]$**: The reaction was carried out under similar conditions outlined for the tungsten analogue using 500 mg of $[Mo_2(O_2C^tBu)_4]$ (0.838 mmol) and 72 mg of $2,5\text{-}Th(CO_2H)_2$ (0.418 mmol). A red solid (435 mg, 90% yield) was isolated by filtration. Microanalysis: Found, C 37.22; H 4.83%. $C_{36}H_{56}O_{16}SMo_4$ requires C 37.26, H 4.86%. NMR (THF-d_8): δ_H (400 MHz) 7.29 (s, 2H, $2,5\text{-}C_4H_2S(CO_2)_2$); 1.43 (s, 18H, $O_2CC(CH_3)_3$); 1.42 (s, 36H, $O_2CC(CH_3)_3$). MALDI-MS: 1162 (100%, M^+), 596 (10%, $[Mo_2(O_2C^tBu)_4]^+$).

‡ $[W_2(3\text{-}ThCO_2)_4]$ did not completely dissolve and thus molar absorptivities would be greater than those reported here.

1 *Handbook of Conducting Polymers*, ed. T. A. Skotheim, R. L. Elsenbaumer and J. R. Reyolds, Second Edition, revised and expanded, 1997.
2 P. Nguyen, P. Gomez-Elipe and I. Manners, *Chem. Rev.*, 1999, **99**, 1515–1548.
3 M. S. Khan, A. K. Kakkar, N. J. Long, J. Lewis, P. Raithby, P. Nguyen, T. B. Marder, F. Wittmann and R. H. Friend, *J. Mater. Chem.*, 1994, **4**, 1227–1232.
4 N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21–38.
5 M. O. Wolf, *Adv. Mater.*, 2001, **13**, 545–553.
6 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, 2nd ed., Oxford University Press, 1993.
7 B. E. Bursten, M. H. Chisholm, C. M. Hadad, J. Li and P. J. Wilson, *Chem. Commun.*, 2001, 2382–2383.
8 B. E. Bursten, M. H. Chisholm, R. J. H. Clark, S. Firth, C. M. Hadad, A. M. MacIntosh, P. J. Wilson, P. M. Woodward and J. M. Zaleski, *J. Am. Chem. Soc.*, 2002, **124**, 3050–3063.
9 A. B. Brignole and F. A. Cotton, *Inorg. Syn. 1971*, 0000, **13**, 81–89.
10 D. J. Santure, J. C. Huffman and A. P. Sattelberger, *Inorg. Chem.*, 1985, **24**, 371–378.
11 R. H. Cayton, M. H. Chisholm, J. C. Huffman and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 1991, **113**, 8709–8724.
12 M. H. Chisholm, B. D. Pate, P. J. Wilson and J. M. Zaleski, *Chem. Commun.*, 2002, 1084–1085.