Concerning the molecular and electronic structure of a tungsten-tungsten quadruply bonded complex supported by two 6-Carboethoxy-2-carboxylatoazulene ligands†

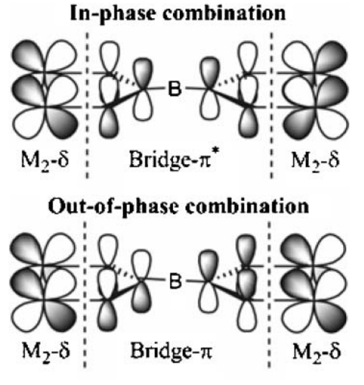
Mikhail V. Barybin,*[a] Malcolm H. Chisholm,*[b] Nathan J. Patmore,[b] Randall E. Robinson[a] and Namrata Singh[b]

Received (in Berkeley, CA, USA) 12th June 2007, Accepted 6th July 2007
First published as an Advance Article on the web 7th August 2007
DOI: 10.1039/b708746b

The preparation and molecular structure of a W_2^{4+}-quadruply bonded complex is reported wherein two mutually *trans* azulene-2-carboxylato ligands are shown to be strongly coupled by ligand π–M_2δ–ligand π conjugation.

Intervalence compounds have two redox active centers (X) connected by a bridge (B) and carry an overall charge such that one center (X) may differ by one unit of charge from the other.[1–3] The redox active units may be metals as in the now classic example of the Creutz–Taube ion,[4] $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ where pz = 1,4-pyrazine, or involve organic groups such as arylamines[5] or tetrathiafulvalenes[6] separated by rigid π-conjugated spacers (*e.g.* phenyl, 4,4-biphenyl, *etc.*). The Robin and Day classification of mixed valency[7] applies equally well to inorganic and organic systems, both of which exhibit similar spectral features in their Class II (strongly coupled) and Class III (fully delocalized) complexes. Furthermore, the mixed valence organic radicals and the mixed valence inorganic complexes both show asymmetric low energy electronic absorptions at the Class II/III border.[8] In most instances, the bridging group serves to couple the redox active centers by π-conjugation though there are examples of where the bridge just serves to bring the redox active centers into direct (through space) coupling as was reported recently by Nelsen for a cyclophane radical cation[9] and by Hupp for a Re_4-containing molecular rectangle with a reduced 4,4-bipyridyl radical.[10]

Recently, we have engaged in extensive studies of the $[M_2]$–B–$[M_2]$ systems where the bridge B is a dicarboxylate ligand and $[M_2]$ represents the MM quadruply bonded groups $\{M_2(O_2CBu^t)_3\}$ of molybdenum and tungsten.[11] In these systems, as also seen by Cotton *et al.* in related formamidinate Mo_2^{4+}-containing dicarboxylate bridged complexes,[12,13] the electronic coupling rapidly falls off with increasing M_2 to M_2 distance and correlates with the extent of coupling between the M_2δ orbitals and the bridge π-system. In a series of related bridged complexes, the electronic coupling is always greater for M = W than for M = Mo because the dominant mode of coupling involves electron transfer *via* the π* orbitals of the bridge and the W_2δ orbitals are roughly 0.5 eV higher in energy than their Mo_2δ analogues.[11,14] With this knowledge in hand, we wondered whether two redox active mutually trans organic groups bonded to a M_2 quadruply bonded center would show strong coupling as a result of ligand π–M_2δ–ligand π conjugation. Schematically, the two systems **I** and **II** illustrated below are complementary in the following manner. In **I**, the bridging dicarboxylate ligand couples two M_2δ orbitals. The $[M_2]_2$δ- to-bridge π* back-bonding provides stabilization of the in-phase combination of the $[M_2]_2$δ orbitals. The dicarboxylate ligand filled π orbital is too low in energy to interact significantly with the out-of-phase combination of the $[M_2]_2$δ orbitals. In **II**, the out-of-phase ligand π* combination interacts with the M_2δ orbital leading to its destabilization (by back-bonding from the metal). The in-phase ligand π* combination does not have the correct symmetry to interact strongly with any of the orbitals in the M_2 manifold. The result of this M_2δ-ligand/bridge π bonding is to cause a splitting of the two M_2δ combinations, the HOMO and HOMO−1, in complexes of type **I** and a splitting of the ligand π* combinations, typically the LUMO and LUMO+1, for type **II** complexes. The magnitude of these splittings measures the strength of the electronic coupling of the redox centers and Class III behavior may arise upon oxidation of **I** or reduction of **II** by one electron.



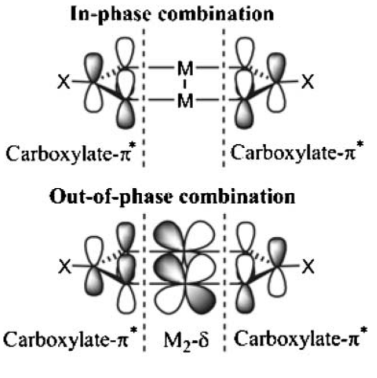
I

Based on our earlier work[15] on azulene-2,6-dicarboxylate bridged complexes, the azulene-2- or 6-carboxylate ligands appeared suitable for study because of their expected small HOMO–LUMO gaps. We also recognized that for tungsten systems the coupling would be greater than for the corresponding molybdenum congeners and further that electronic structure

---

[a] *Department of Chemistry, The University of Kansas, 1251 Wescoe Hall Drive, Lawrence, Kansas, 66045-7582, USA*
[b] *Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio, 43210-1185, USA. E-mail: Chisholm@chemistry.ohio-state.edu*

† Electronic supplementary information (ESI) available: experimental details, computational procedures, MO diagram and Gausview orbital plots, electrochemical data and details of the X-ray determination. See DOI: 10.1039/b708746b



II

calculations would be valuable in guiding selection of the target molecule having the desired electronic structure. In order to keep close analogy with our earlier work,[15] we considered the use of azulene-2,6-substituted carboalkoxy-carboxylates. Electronic structure calculations employing the Gaussian suite of programs[16] on the model ditungsten complexes *trans*-$W_2(O_2CH)_2(Azu\text{-}2')_2$ (Azu-2′ = azulene-6-carbomethoxy-2-carboxylate) and *trans*-$W_2(O_2CH)_2(Azu\text{-}6')_2$ (Azu-6′ = azulene-2-carbomethoxy-6-carboxylate) indicated that the Azu-2′ complex should exhibit greater coupling. As shown in the MO energy level diagram depicted in Fig. S1†, the $W_2\delta$ orbital is stabilized by $M_2\delta$ to ligand π* back-bonding and the LUMO and LUMO+1, both of which are ligand-based, show greater energy separation for Azu-2′. Selected Gaussview plots of the frontier molecular orbitals are also provided in Fig. S1 (See Supplemental Information†). The HOMO is clearly a metal-centered δ orbital with a small degree of mixing with the out-of-phase combination of the azulenic π* orbitals. The LUMO and LUMO+1 are the in-phase and out-of-phase combinations of azulenic π* orbitals, respectively, with the LUMO+1 being raised in energy as a result of mixing with the $M_2\delta$ orbital. The HOMO−1 and HOMO−2 are essentially isoenergetic and constitute the in-phase and out-of-phase combinations of the ligands' highest occupied π-orbitals located on the azulenic rings.

For synthetic considerations, azulene-6-carboethoxy-2-carboxylic acid was employed. Reaction of 2 equiv. of this acid with $W_2(TiPB)_4$ in toluene afforded the pale green complex *trans*-$W_2(TiPB)_2(Azu\text{-}2)_2$, where TiPB is the bulky 2,4,6-triisopropylbenzoate ligand and Azu-2 is the 6-carboethoxy-2-carboxylato ligand. The molecular structure of this compound deduced from a single crystal X-ray structure determination[17] is shown in Fig. 1. The central $W_2(O_2C)_4$ paddle-wheel unit has the expected geometry[11] and the *trans*-configuration of the molecule stems from the sterically preferential disposition of the two bulky TiPB groups. The aryl groups of the TiPB ligands are *twisted ca.* 90° with respect to the corresponding CO_2 moieties, whereas the azulenic rings and the attendant 6-carboethoxy groups are *coplanar* with the 2-carboxylate fragments. This geometry optimizes $M_2\delta$ to azulene π-conjugation and sets up the azulene π-to-π coupling *via* the M_2 center. The ^1H NMR spectrum of the product also supports existence of one dominant isomer in solution. The lack of evidence of diastereotopic methyl groups within the isopropyl substituents is consistent with the *trans*- rather than *cis*-geometry. Yet, the NMR data can not unambiguously rule out the presence of a minor *cis* isomer in solution masked by a rapid interconversion of *cis* and *trans*-configurations. However, this type of rapid isomerization is not commonly observed for complexes of the type $Mo_2(O_2CR)_2(O_2CR')_2$, though they are known to be chemically labile on a slower time scale.[18]

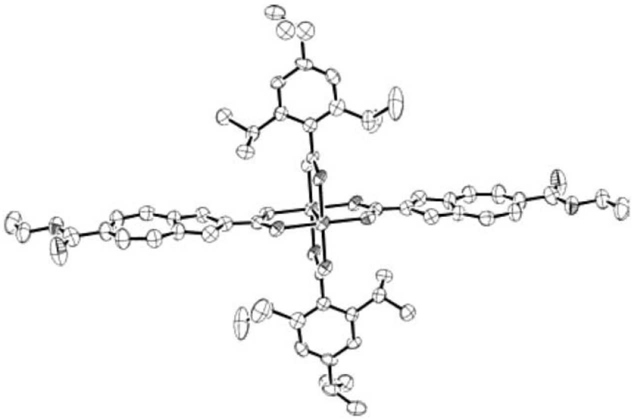


Fig. 1 An ORTEP drawing of the $W_2(TiPB)_2(2\text{-}CO_2\text{-}6\text{-}EtO_2C\text{-}azulene)_2$ molecule seen in the solid-state. Thermal ellipsoids are drawn at the 50% probability level.

The electronic absorption spectrum of the title compound is shown in Fig. 2 along with that of the previously described azulene-2,6-dicarboxylate bridged compound $[W_2(O_2CBu^t)_3]_2$-(μ-2,6-$(CO_2)_2$-$C_{10}H_6$), W_4Azu.[15] These spectra are very similar and the dominant feature is a strong absorption band (ε > 50,000 $M^{-1}cm^{-1}$) centered at 1,100 nm, which in both cases is assigned to the $M_2\delta$ to azulene-carboxylate π* LUMO transition.

The electronic spectrum of the $W_2(TiPB)_2(Azu\text{-}2)_2^-$ anion, formed upon reduction of its neutral precursor with cobaltocene, and that of the radical cation of the azulenedicarboxylate bridged complex, W_4Azu^+, show remarkable similarity as well (Fig. 3). Both exhibit intense absorptions at ∼1,100 nm due to $M_2\delta$ to azulene π* transitions. In addition, in the infrared region, ∼3000 cm^{-1}, there is a low energy asymmetric band. In the case of the W_4Azu^+ complex, this feature is assigned as a charge resonance band involving the singly occupied HOMO and HOMO−1. For $W_2(TiPB)_2(Azu\text{-}2)_2^-$, we suggest this transition involves the coupled ligand-centered radical, *i.e.*, the band arises

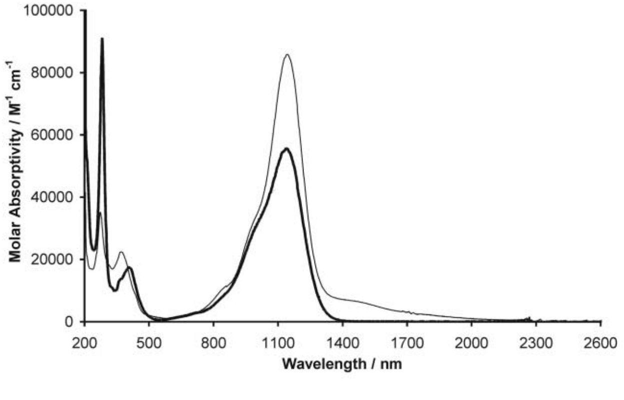


Fig. 2 UV/Vis spectrum of $W_2(TiPB)_2(2\text{-}CO_2\text{-}azulene\text{-}6\text{-}CO_2Et)_2$ in THF at room temperature (bold trace), compared to that of W_4AZU (light trace).

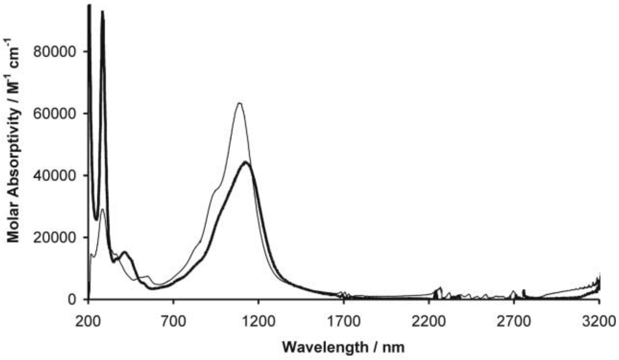


Fig. 3 UV/Vis spectrum of $W_2(TiPB)_2(2\text{-}CO_2\text{-Azulene-6-}CO_2Et)_2^-$ in THF at room temperature (bold trace), compared to that of W_4AZU^+ (light trace).

from excitation from the now singly occupied orbital analogous to the LUMO shown in Fig. S1† to the LUMO+1-like orbital.

Whereas the W_4Azu^+ cation gives an EPR signal with $g \sim 1.8$ and hyperfine coupling to two different sets of the W_2 units (^{183}W, $I = ½$, 15% nat. abund.), the spectrum of $[W_2(TiPB)_2(Azu)_2]^-$ in 2-methyltetrahydrofuran at 223 K shows a relatively sharp signal with $g = 2.0$ and no evidence of hyperfine coupling. This observation is consistent with a ligand-centered radical for the latter species.

Cyclic voltammogram of the title complex features a reversible oxidation wave at −0.45 V (*vs.* $Cp_2Fe^{0/+}$) corresponding removal of an electron from the W_2 δ orbital. The first two reduction waves at −1.50 V and −1.86 V are assigned to the reduction of the azulene-carboxylate ligands, although their irreversible nature precludes determination of the comproportionation constant, K_c.

In conclusion, we propose that the above preliminary results support the complementary nature of the complexes of types **I** and **II** upon oxidation and reduction, respectively, that arises from $M_2\delta$ to ligand π conjugation. This behavior is particularly relevant to developing an understanding of optoelectronic properties of conjugated organic polymers incorporating MM quadruple bonds,[19] which may undergo hole transport upon oxidation and electron transport upon reduction along with other interesting properties such as electroluminescence and photon harvesting.

We thank the National Science Foundation for support of this work and the Ohio Super Computer Center for resource units.

Notes and references

1 S. F. Nelsen, *Chem.–Eur. J.*, 2000, **6**, 581.
2 J.-P. Launay, *Chem. Soc. Rev.*, 2001, **30**, 386.
3 B. S. Brunschwig, C. Creutz and N. Sutin, *Chem. Soc. Rev.*, 2002, **31**, 168.
4 C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1969, **91**, 3988.
5 C. Lambert and G. Noll, *J. Am. Chem. Soc.*, 1999, **121**, 8434.
6 K. Lahlil, A. Moradpour, C. Bowlas, F. Menou, P. Cassoux, J. Bonvoisin, J.-P. Launay, G. Dive and D. Dehareng, *J. Am. Chem. Soc.*, 1995, **117**, 9995.
7 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.
8 K. D. Demadis, C. M. Hartshorn and T. J. Meyer, *Chem. Rev.*, 2001, **101**, 2655.
9 S. F. Nelsen, A. E. Konradsson and J. P. Telo, *J. Am. Chem. Soc.*, 2005, **127**, 920.
10 P. H. Dinolfo and J. T. Hupp, *J. Am. Chem. Soc.*, 2004, **126**, 16814.
11 M. H. Chisholm and N. J. Patmore, *Acc. Chem. Res.*, 2007, **40**, 19.
12 F. A. Cotton, J. P. Donahue and C. A. Murillo, *J. Am. Chem. Soc.*, 2003, **125**, 5436.
13 F. A. Cotton, J. P. Donahue, C. A. Murillo and L. M. Perez, *J. Am. Chem. Soc.*, 2003, **125**, 5486.
14 M. H. Chisholm, R. J. H. Clark, J. C. Gallucci, C. M. Hadad and N. J. Patmore, *J. Am. Chem. Soc.*, 2004, **126**, 8303.
15 M. V. Barybin, M. H. Chisholm, N. S. Dalal, T. H. Holovics, N. J. Patmore, R. E. Robinson and D. J. Zipse, *J. Am. Chem. Soc.*, 2005, **127**, 15182.
16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03*, Gaussian, Inc., Pittsburgh, PA, 2003.
17 Crystallographic data for $W_2(TiPB)_2(Azu\text{-}2)_2\cdot 2THF$: $C_{68}H_{84}O_{14}W_2$, $M = 1493.05$, triclinic. $a = 10.358(3)$, $b = 10.563(3)$, $c = 17.222(7)$ Å, $\alpha = 106.775\ (10)^\circ$, $\beta = 93.233(10)^\circ$, $\gamma = 114.97(2)^\circ$, $V = 1600.6(10)$ Å^3, $T = 150(2)$ K, $Z = 1$, $\mu = 3.654$ mm^{-1}, $F_{000} = 752$, Final $R1 = 0.0475$, $wR2 = 0.0883$ with $I > 2\sigma(I)$, GOF = 0.994 for 380 parameters and a total of 14874 reflections of which 4440 were independent ($R_{int} = 0.086$). CCDC 622539†.
18 R. H. Cayton, S. T. Chacon, M. H. Chisholm and K. Folting, *Polyhedron*, 1993, **12**, 415.
19 M. H. Chisholm, A. J. Epstein, J. C. Gallucci, F. Feil and W. Pirkle, *Angew. Chem., Int. Ed.*, 2005, **44**, 6537.