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Molecular and electronic structure of MM quadruply bonded complexes containing $O_2CC_6H_4N(Ph)_2$ supporting ligands

Malcolm H. Chisholm *, Christopher B. Durr, Sharlene A. Lewis

Department of Chemistry and Biochemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH 43210, USA

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The complexes *trans*-$M_2(T^iPB)_2(O_2CC_6H_4\text{-}4\text{-}NPh_2)_2$ where M = Mo (**I**), and M = W (**II**) were prepared from the reaction between $M_2(T^iPB)_4$ and the carboxylic acid $Ph_2N\text{-}4\text{-}C_6H_4CO_2H$ (~2 equiv.) in toluene (T^iPB = 2,4,6-triisopropylbenzoate). The compounds were isolated as microcrystalline powders that are yellow, **I** or purple **II**, and are air-sensitive. Compound **I** was characterized by single-crystal X-ray crystallography and shown to have a centrosymmetric structure and a planar central $C_6H_4\text{-}CO_2M_2O_2C\text{-}C_6H_4$ unit. Calculations indicate that the HOMO is principally $M_2\delta$ with mixing of the filled π-orbitals of the N,N-diphenyl-4-aminobenzoate. Oxidation of **I** and **II** yield cationic species that have been characterized by EPR and UV–Vis–NIR spectroscopy. The radical cations show EPR spectra characteristic of M_2^{5+} centers having the MM configuration $\sigma^2\pi^4\delta^1$ and compound $\mathbf{I}^+$ shows a low energy NIR transition assignable to a ligand to metal charge transfer transition. The homoleptic compound $Mo_2(O_2CC_6H_4\text{-}4\text{-}N\text{-}Ph_2)_4$, **III**, was prepared from the reaction between $Mo(CO)_6$ and $Ph_2N\text{-}4\text{-}C_6H_4CO_2H$ in refluxing *ortho*-dichlorobenzene and is shown to exhibit similar spectroscopic features to those of **I**.

1. Introduction

Mixed valence molecular species arise when two redox active metal centers are linked by a bridging group and there is an overall odd charge. In inorganic chemistry this has been a topic of considerable interest for over four decades and the Creutz-Taube ion [1] $[(NH_3)_5\text{-}Ru(\mu\text{-pyrazine})Ru\text{-}(NH_3)_5]^{5+}$ represents perhaps the classic case for the question of where the odd positive charge rests. On the Robin and Day classification [2] a fully delocalized ion, one where the two redox centers share the odd charge equally, is class III while one where the charge is trapped is class I. Class II represents a situation where the charge is localized, but thermal energy or light may induce charge transfer. The two redox centers are to some degree coupled electronically. Here Hush theory [3] predicts the appearance of an optical transition that is solvent dependent; since this inter-valence charge transfer, IVCT, is photoinduced and is accompanied by a dipole change. As the electronic coupling becomes stronger the energy required to promote this electron exchange becomes less and the distinction between class II and class III becomes a matter of the timeframe of the experimental technique employed. Indeed, much attention in the past decade has been directed to the study of mixed valence, MV, ions that are close to this II/III border. The optical properties of these ions have distinct features. [4] Also the rate of electron exchange can be monitored on the IR time-scale in certain instances and, as Kubiak has shown, may be both solvent and temperature dependent [5,6].

Although major attention has been devoted to inorganic systems, the phenomenon is common to organic chemistry and some prime examples of recent studies are shown in Scheme 1. The amine based cations have been extensively studied by Lambert [7] and the anions by Nelsen et al. [8]. The 1,4-phenylene bridged cation represents a relatively rare example of a fully delocalized organic cation and this probably accounts for the fact that N,N′-tetraaryl-1,4-phenylenediamines are employed in optoelectronic devices as hole transport materials [9].

We have recently been employing MM quadruply bonded units to study the properties of MV ions close to the II/III border [10]. Compounds of the form $[M_2]\text{-}L\text{-}[M_2]$ and *trans*-L-M_2-L, where "L" represents a conjugated organic group coupled to the M_2 center(s), provide upon oxidation and reduction, respectively, MV ions that are metal or ligand centered. The spectral feature of the anions formed upon reduction of the isonicotinate complexes *trans*-$M_2(T^iPB)_2[O_2CC_5H_4N\text{-}B(C_6H_5)_3]_2$ where T^iPB = 2,4,6-triisopropylbenzoate are shown in Fig. 1 and represent MV anions that are class III (fully delocalized) for M = W and close to the II/III border for M = Mo [11]. Following this earlier study we were curious concerning the possible nature of the dimetallated amine shown schematically in Scheme 2 below in relation to the phenylenediamine cation shown in Scheme 1. We describe here our preparation of both the bis–bis complexes *trans*-$M_2(T^iPB)_2[O_2CC_6H_4\text{-}4\text{-}N(Ph)_2]_2$ (where M = Mo and W) and the homoleptic complex $Mo_2[O_2CC_6H_4\text{-}4\text{-}N(Ph)_2]_4$ together with their electrochemical and spectroscopic properties.

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* Corresponding author. Tel.: +1 614 688 3625; fax: +1 614 292 0368.
E-mail address: chisholm@chemistry.ohio-state.edu (M.H. Chisholm).

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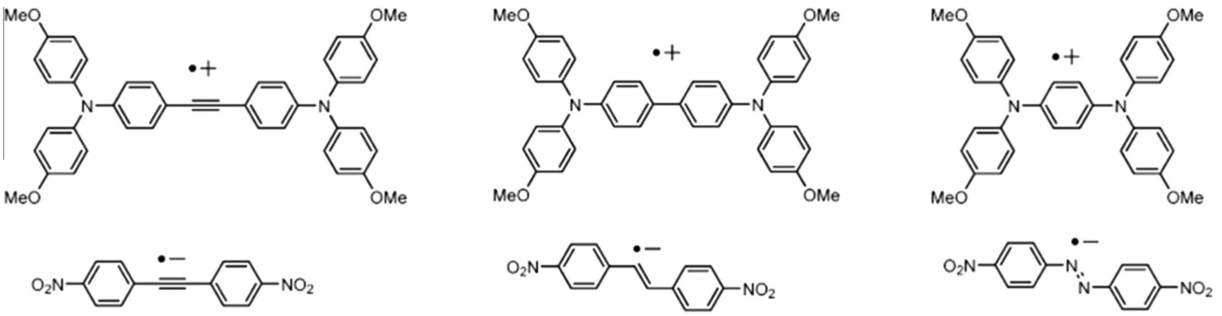


Scheme 1. Organic mixed valence systems.

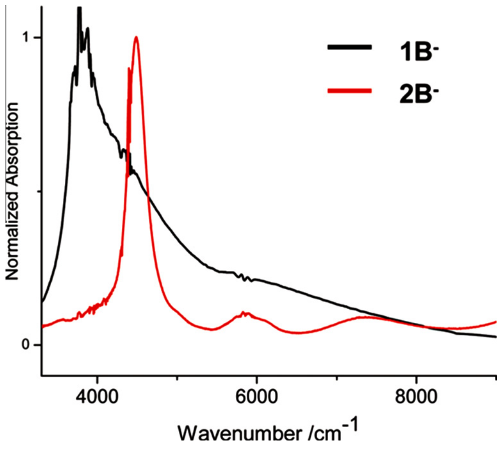
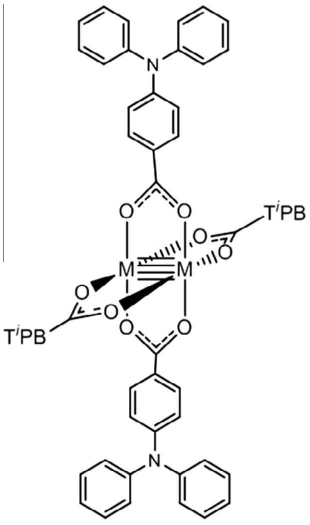


Fig. 1. Taken from reference [10]Spectral features of reduced *trans*-$M_2(T^iPB)_2[O_2CC_5H_4N\text{-}B(C_6H_5)_3]_2$ where M = Mo (black) and M = W (red). (Color Online.)



Scheme 2. Structure of the dimetallated amine.

2. Materials and methods

2.1. NMR

NMR spectra were recorded on a 400 MHz Bruker DPX Advance 400 spectrometer. All ^1H NMR chemical shifts are in ppm relative to the protio impurity in THF-d_8 at 3.58 ppm.

2.2. Electronic absoption spectra

UV–Vis–NIR electronic spectra in THF solutions were measured at room temperature using a Perkin–Elmer Lambda 900 spectrometer.

2.3. Electrochemical studies

Cyclic voltammograms were collected at a scan rate of 50 mV/s using a Princeton Applied Research (PAR) 173A potentiostat-galvanostat equipped with a PAR 176 current-to-voltage converter. The measurements were performed under an argon atmosphere in a 0.1 M solution of $^nBu_4NPF_6$ in THF or CH_2Cl_2 inside a single-compartment voltammetry cell that was equipped with a platinum wire auxiliary electrode, a platinum working electrode and a pseudoreference electrode consisting of a silver wire in 0.1 M $^nBu_4NPF_6$/THF or 0.1 M $^nBu_4NPF_6/CH_2Cl_2$ separated from the bulk solution by a Vycor tip. The potentials are referenced to the Cp_2Fe/Cp_2Fe^+ couple.

2.4. Mass spectrometry

Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Microflex mass spectrometer. Dithranol was used as the matrix.

2.5. Electronic structure calculations

The model complexes were optimized in the gas-phase using density functional theory (DFT) utilizing the GAUSSIAN09 suite of programs [12,13]. The B3LYP [14,15] functional was used in conjunction with the SDD energy consistent pseudopotentials and the SDD energy consistent basis set for for molybdenum and tungsten and the 6-31G$*$ basis set for H, C, N and O atoms. Vibrational frequency analysis was used to confirm that the optimized structures were minima on the potential energy surface. GAUSSVIEW isosurface contour plots are shown with an isovalue of 0.02 [15]. Electronic absorption spectra were calculated using the time dependent DFT (TDDFT) method.

2.6. Crystallographic information

Single crystals of **I** were isolated as bright yellow plates and handled under a pool of fluorinated oil. Examination of the diffraction pattern was done on a Nonius Kappa CCD diffractometer with Mo Kα radiation. All work was done at 200 K using an Oxford Cryosystems Cryostream Cooler.

Data integration was done with Denzo, and scaling and merging of the data was done with Scalepack [16]. The structure was solved by the direct methods program in SHELXS-97 [17]. Full-matrix least-squares refinements based on F^2 were performed in SHELXL-97, as