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Heterometallic Multiple Bonding: Delocalized Three-Center σ and π Bonding in Chains of 4d and 5d Transition Metals

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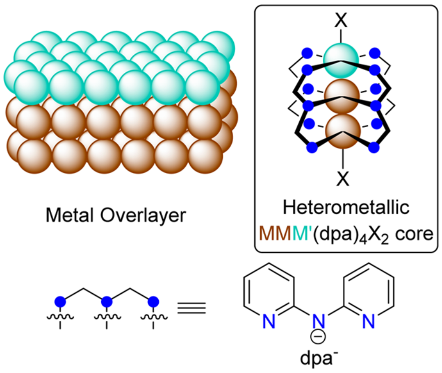
S Supporting Information

ABSTRACT: Heterotrimetallic compounds $Mo_2Ru(dpa)_4Cl_2$ (**1**) and $W_2Ru(dpa)_4Cl_2$ (**2**) are prepared by reactions of $M_2(dpa)_4$ (M = Mo or W; dpa = 2,2′-dipyridylamide) with $[Ru(CO)_3Cl_2]_2$. Crystallographic studies reveal short Mo−Ru and W−Ru distances, 2.38 Å (**1**) and 2.39 Å (**2**), suggestive of delocalized Mo−Mo−Ru and W−W−Ru bonding. In contrast to the σ bonding found in the corresponding iron compounds, density functional theory calculations reveal both a three-center/two-electron σ bond and two three-center/four-electron π bonds in the M−M−Ru compounds.

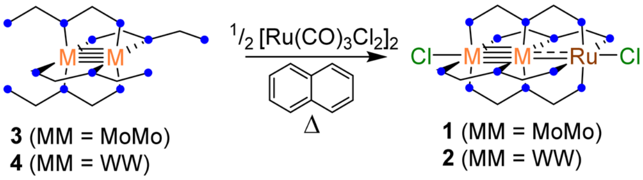
Small one-dimensional metal-atom chain compounds are of great interest for potential utility in electron-transport materials, as well as for probing fundamental questions on the nature of metal−metal bonds.[1] Additionally, we may consider a heterotrimetallic chain, M−M−M′, to represent the smallest possible model for bonding in metal overlayers on surfaces that have considerable importance to heterogeneous catalysis (Chart 1).[2] Heterotrimetallic M−M−M′ compounds prepared by us[3] or others[4] in the past have always contained at least one first-row transition metal, which because of the smaller size of 3d orbitals has limited the possibility of heterometallic electron delocalization to partial σ-type interactions via a three-center/three-electron (3c/3e) σ bond with heterometallic M−M′ bond distances of over 2.5 Å. The Mashima group has been able to construct M′−Mo≡Mo−M′ chains that incorporate second-row d^7 or d^9 heterometals at each terminus, which also results in multicenter σ bonding; in these cases, the Mo−M′ distances are close to 2.7 Å.[5] We report here the first example in which a second-row d^6 ion, Ru^{II}, can be appended to a multiply bonded M_2 unit at distances shorter than 2.4 Å, resulting in the first heterotrimetallic chain complexes that do not include first-row transition metals and the first for which multicenter π bonding (in addition to σ bonding) plays a role.

Chart 1. Heterotrimetallic M−M−M′ Chain Compounds as Models for Bonding in Metal Overlayers



The synthetic strategy to form $Mo_2Ru(dpa)_4Cl_2$ (**1**; dpa = 2,2′-dipyridylamide) and $W_2Ru(dpa)_4Cl_2$ (**2**) required an approach different from that of compounds with 3d transition metals appended to a Mo_2 or W_2 quadruply bonded unit, which are formed by the simple addition of a metal(II) dichloride to the bimetallic quadruply bonded compound at elevated temperatures.[3c−e] We initially tested $Ru(DMSO)_4Cl_2$ (DMSO = dimethyl sulfoxide) as a "$RuCl_2$" equivalent with no success, observing instead only mononuclear $Ru(dpa)_3$ species by MALDI-TOF mass spectrometry, due to the presence of liquid DMSO in the reaction solution. In order to avoid this problem, the tricarbonyldichlororuthenium dimer, $[Ru(CO)_3Cl_2]_2$, was used with the expectation that the expelled CO ligands would not adversely affect the reaction. The reaction of $Mo_2(dpa)_4$ (**3**) with 0.5 equiv of $[Ru(CO)_3Cl_2]_2$ in refluxing naphthalene yielded the desired heterotrimetallic compound **1** (Scheme 1) in useful yield.

Scheme 1. Syntheses of Compounds 1 and 2



The analogous compound, **2**, can be prepared similarly but in lower yield because a significant amount of $[W_2(dpa)_3Cl_2]^+$ byproduct[6] is observed in the mass spectra.

Compounds **1** and **2** both crystallize in the monoclinic space group $P2_1/c$ with two independent trimetallic molecules in the asymmetric unit (Figure 1 and Table S1 and Figure S1 in the Supporting Information, SI). Compounds **1** and **2** possess minor disorder in the metal-atom positions, with the M−M−Ru unit ordered in two opposite directions.[7] The average Mo−Mo bond distances in **1** are 2.123 Å, which are only slightly longer than the quadruple bond distances in **3**, 2.097 Å. The W−W bond distances, 2.193 Å, are equivalent to the distance in **4**, 2.193 Å.[3c,6] The distances to the Ru^{II} ion in **1** are 2.384 and 2.390 Å in **2**

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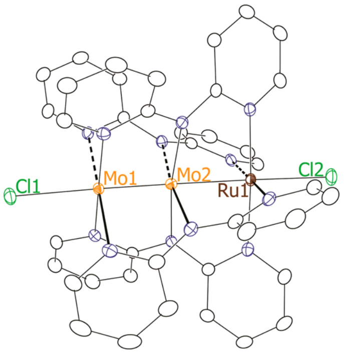

Figure 1. Crystal structure of **1** with ellipsoids drawn at the 50% level. Only one molecule from the asymmetric unit is shown. H atoms have been omitted for clarity.

(Table S2 in the SI). These heterometallic Mo−Ru and W−Ru distances are notably shorter than the sum of the single-bond covalent radii of these elements (Mo−Ru, 2.63 Å; W−Ru, 2.62 Å)[8] but just above the sums of the double-bond covalent radii (Mo═Ru, 2.35 Å; W═Ru, 2.34 Å).[9]

There are only two reports of Mo−Ru distances shorter than that observed in **1**. Collman et al. reported on two isomeric metalloporphyrin dimers with Mo−Ru multiple bond distances of 2.211 and 2.181 Å,[10] described as having metal−metal bond orders of 2.5 and 3.5, respectively. To our knowledge, the W−Ru distance in **2** is the shortest reported to date. Complexes with Mo (W)−Ru distances similar to those observed in **1** or **2** feature bridging carbonyl ligands, hydrides,[11] or carborane clusters,[12] for which the Mo (W)−Ru bonding was not described. It is apt to compare the distances in **1** and **2** with those of the corresponding first-row analogues, $Mo_2Fe(dpa)_4Cl_2$ (**5**) and $W_2Fe(dpa)_4Cl_2$ (**6**), which we recently reported.[3e] In **5** and **6**, the Fe^{II} ions are high-spin, and the Mo (W)−Fe distances are long, ∼2.7 Å. Thus, the shorter Mo (W)−Ru distances in **1** and **2** indicate, first, that Ru^{II} is low-spin and also that there is a greater degree of heterometallic bonding in the ruthenium complexes.

The ^1H NMR spectra of **1** and **2** show eight and four resonances in the aromatic region (Figure S2 in the SI), respectively, with several signals in **1** overlapping, signifying the following: (1) The compounds are diamagnetic. (2) Despite the differing identity of the metal atoms at each end of the heterometallic chain, the corresponding H atoms on the two pyridine rings of dpa display very similar chemical shifts for **1** and are equivalent for **2**. This observation further suggests electron delocalization throughout the heterometallic chain.

The cyclic voltammograms for **1** and **2** in dichloromethane are shown in Figure S3. Both compounds display a reversible $[M_2Ru]^{6+/7+}$ feature at $E_{1/2} = -0.543$ V for **1** and $E_{1/2} = -0.892$ V for **2**, followed by a second quasireversible $[M_2Ru]^{7+/8+}$ feature at $E_{1/2} = 0.641$ V for **1** and $E_{1/2} = 0.124$ V for **2**. Qualitatively similar electrochemical features are observed for **5** and **6**, with the following exceptions: (1) Oxidation from $[M_2Fe]^{7+}$ to $[M_2Fe]^{8+}$, believed to be Fe-centered, is irreversible, demonstrating a kinetic instability of the Fe(III) complexes and therefore a corresponding relative stability of the Ru complexes. (2) In **5** and **6**, $[M_2Fe]^{6+/7+}$ oxidation, attributed to oxidation of the M_2 quadruple bond, shifts 440 mV more negative upon substitution of Mo for W,[3e] similar to the 350 mV shift in the $[M_2Ru]^{6+/7+}$ wave observed for **1** and **2**. There is, however, less of a shift (∼220 mV) in the $Fe^{2+/3+}$ potential,[3e] whereas the $[M_2Ru]^{7+/8+}$ wave shifts by ∼520 mV in the W-containing compound. These results are in line with the charge being more delocalized in the Ru compounds.

Density functional theory (DFT) calculations provide a means to further probe the M−Ru bonding within **1** and **2** via a comparison to the Fe complexes **5** and **6** (Table S2 in the SI). A comparison of DFT-derived molecular orbital diagrams for **5** and **1** is given in Figure 2. Spin polarization within the open-shell **5** is denoted by the differing energies of the α- and β-spin orbitals that contain the unpaired electrons of the compound. In both **1** and **5**, a set of delocalized three-center σ-type orbitals are seen from the calculations (σ, σ_{nb}, and σ^*, all of a symmetry in the C_4 point group; Figure S4 in the SI). Notably, for **5**, the σ orbital is filled, with σ_{nb} containing one of the unpaired electrons, thus forming a

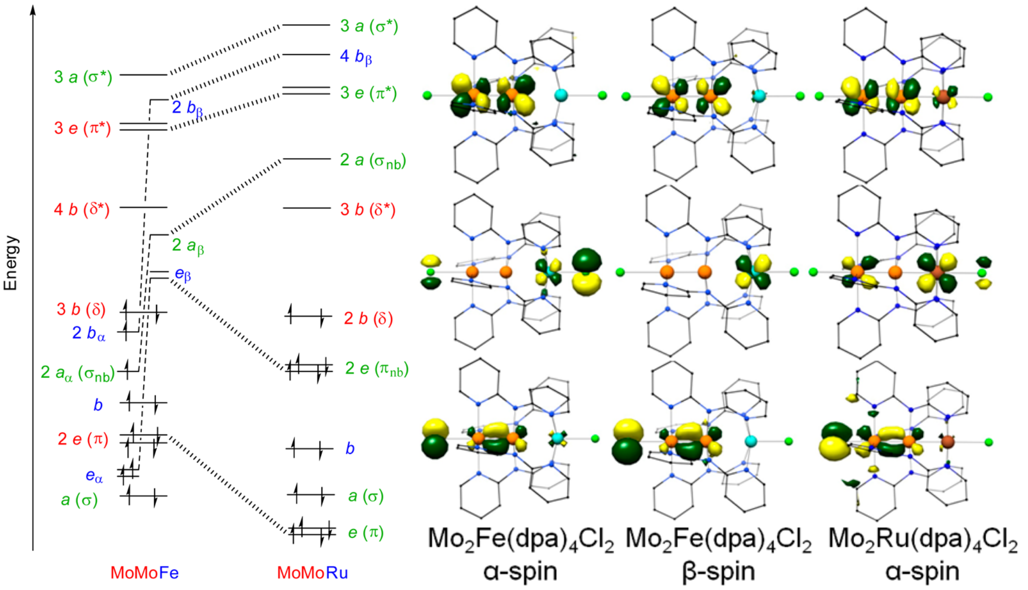

Figure 2. (left) Comparison of molecular orbital diagrams for **5** (left) and **1** (right). Orbitals localized on the Mo_2 unit are given with red labels, blue labels represent Fe- or Ru-centered orbitals, and the green labels indicate orbitals that show significant delocalization throughout the Mo−Mo−M chain. (right) Comparison of π-type orbitals for **5** (left and center) and **1** (right).

3c/3e σ bond that spans the entire heterometallic chain. In contrast, σ_{nb} is empty in **1**, being pushed to higher energy by the larger ligand-field splitting of the Ru atom. Thus, a 3c/2e σ interaction exists in **1**.

The e symmetry π-bonding orbitals are shown to the right in Figure 2. In both **1** and **5**, the lowest-energy doubly occupied e symmetry π-bonding orbitals are mainly localized on the Mo_2 unit but are lowered in energy for **1** because of the added Ru character of ~11%. The next set of e orbitals shows the largest difference between **1** and **5**. In the Fe complex, these house two of the unpaired electrons of the compound and are essentially localized on Fe, with no contribution from the Mo atoms. In the Ru complex, the 2e orbitals are also clearly polarized toward Ru but have considerable contribution, 23%, from the distal Mo atom in the manner of a classical three-center nonbonding orbital. Also, in the antibonding π^*, 3e, the orbitals for **5** are essentially localized Mo_2 π^* orbitals, while **1** shows distinct three-center character.

The increased electron delocalization in **1** and **2** compared to that in **5** and **6** is manifested in the Mayer bond order (MBO) values for the compounds (Table S3 in the SI). The MBO between the M_2 unit and the appended M^{II} ion is much higher for **1** and **2** than for **5** and **6**, and as a consequence, the MBO value for the Mo−Mo or W−W bonds is smaller for **1** and **2** compared to that for **5** and **6**. Moreover, the Ru−Mo MBO value greater than 1.00 indicates clearly partial multiple bond character via both σ and π bonding. The substantial M_{outer}−Ru bond orders are also a good indicator of the three-center character of the bonding.

While the σ and π orbitals in **1** and **2** are delocalized, there is less delocalization of the orbitals of δ (b) symmetry. Thus, the highest occupied and lowest unoccupied molecular orbitals of **1** and **2** are essentially the M_2 δ and δ^* orbitals. As such, the lowest-energy absorptions of **1** (630 and 733 nm) and **2** (685 nm) (Figure S5 in the SI) may be assigned to M_2 $\delta \rightarrow \delta^*$ transitions, as in **5** and **6**. The results of time-dependent DFT calculations agree with this assessment and also show a mixing of metal-to-metal or metal-to-ligand charge-transfer character in this band in the case of **1** and **2**, respectively (Figure S6 in the SI). The higher-energy bands in the visible spectrum are charge-transfer bands.

We have described the synthetic breakthroughs that allow for the synthesis of the first asymmetric heterotrimetallic complexes supported by the dpa ligand containing only 4d or 5d metals, **1** and **2**. These compounds exhibit very short M−Ru distances, which leads to significant electron delocalization along the M−M−Ru core. DFT calculations show that there is a 3c/2e σ bond and two 3c/4e π bonds that contribute to the electronic structure. In contrast to the corresponding Fe compounds, which show irreversible electrochemical features, the Ru species show multiple reversible waves. Thus, it may be possible to use **1** and **2** to model multielectron reactions such as those catalyzed by mixed Mo/Ru or W/Ru surfaces.[13]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, synthesis, crystallography, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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