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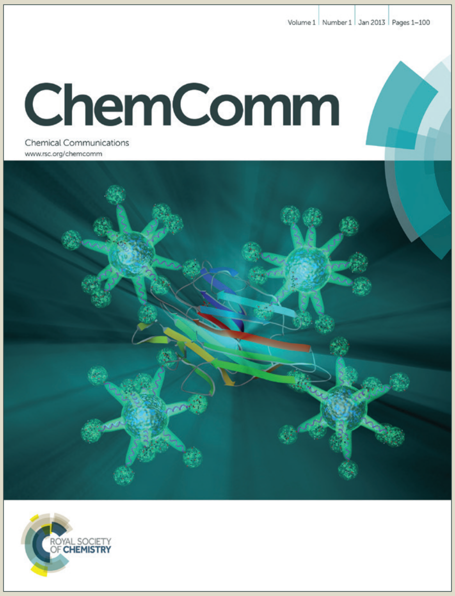

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An Unsupported Metal Hydroxide for the Design of Molecular μ-Oxo Bridged Heterobimetallic Complexes

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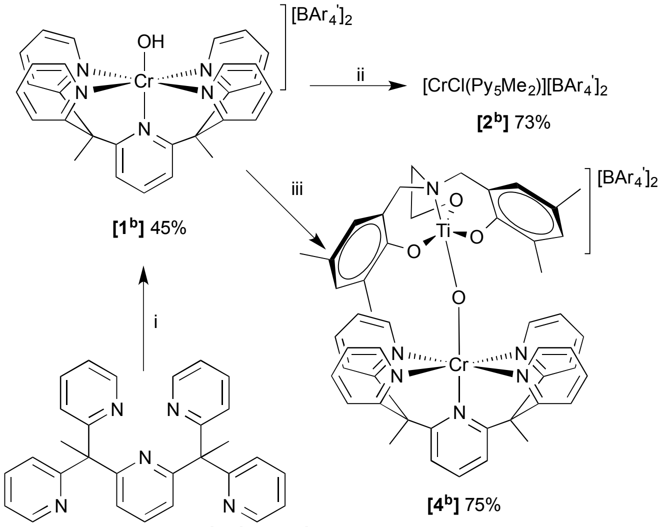
A terminal and unsupported chromium(III) hydroxide is reported. The terminal hydroxide is used to synthesize the first example of a heterobimetallic Ti-O-Cr compound containing an unsupported μ-oxo bridge. The heterobimetallic complex exhibits a new absorbance at 288 nm (4.32 eV), which is assigned to a metal-to-metal charge transfer (MMCT) transition.

The reactivity of terminal metal hydroxides is of interest for the synthesis of heterobimetallic compounds[1,2] and for modelling enzyme active sites.[3,4] Heterobimetallic, μ-oxo bridged, first row transition metals are known to use MMCT to drive photochemical fuel production in the solid state.[5] However, the ability to both coarsely (~V) and finely (~mV) tune the redox potentials of the donor and acceptor metals in such systems remains elusive. Here we report the synthesis of the first member of a new class of molecular μ-oxo bridged heterobimetallic molecules, containing M^{III} (Cr^{III}) electron donors and a Ti^{IV} electron acceptor. Molecules of this type exhibit a new electronic transition, attributed to the MMCT between donor and acceptor. The redox potentials of such molecules can be modified through both ligand and metal variations.[6-8]

As shown in Scheme 1, metallation of the Py_5Me_2 ligand with anhydrous $CrCl_2$ in acetonitrile (1:1) followed by reaction with excess water results in $[CrOH(Py_5Me_2)]^{2+}$ (**1**^{a}) in high yield prior to anion exchange (90%). A biphasic mixture of diethyl ether and water (1:1) was used to exchange chloride with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [BAr_4'], which results in $[CrOH(Py_5Me_2)^{2+}$ (1^b), (45%). By Evans' method, **1**^{b} has a effective magnetic moment, $\mu_{eff} = 3.42\ \mu_{BM}$, characteristic of a high-spin Cr^{III} stabilized by a pentadentate polypyridyl ligand.[9] Dark purple crystals of **1**^{b} were obtained by layered diffusion of *n*-pentane into a diethyl ether solution. The single crystal X-ray structure of **1**^{b} shows an axial hydroxide ligand with a Cr-O bond length of 1.87 Å. This bond length is comparable to other Cr^{III} hydroxides, and considerably shorter than Cr^{III} aquo complexes in similar ligand environments.[10-12] The average equatorial Cr-N bond length is 2.07 Å, whereas the axial Cr-N bond length is 2.09 Å. The presence of a terminal hydroxide was further confirmed by treatment of crude $[CrCl(Py_5Me_2)]^{1+}$ with D_2O. ($\nu_{OD} = 2690\ cm^{-1}$ vs. $\nu_{OH} = 3647\ cm^{-1}$). The relatively weak intensity of ν_{OH} is consistent with other terminal hydroxides reported by Goldsmith and Stack.[4]



Scheme 1 Synthesis of **1**^{b}, **2**^{b}, and **4**^{b}. i.) Anyhd. $CrCl_2$, MeCN, 72 h followed by H_2O and anion exchange with [BAr_4'] ii.) **1**^{b}, THF, TMS-Cl, 24 h, r.t. iii.) **1**^{b}, THF, **3**, 48 h, r.t.

To determine if the hydroxide in complex **1**^{b} is labile, **1**^{b} was treated with excess chlorotrimethylsilane (TMS-Cl) in tetrahydrofuran at room temperature, followed by repeated washing with hexanes. This results in $[CrCl(Py_5Me_2)]^{2+}$ (**2**^{b}) as a fine, pink powder (73%). The high-spin Cr^{III} center was preserved in this reaction ($\mu_{eff} = 3.44\ \mu_{BM}$). Dark pink crystals suitable for diffraction were obtained via vapor diffusion of *n*-pentane into a dichloromethane solution. (See ESI for full structural information) The Cr-Cl bond length of 2.26 Å in **2^b** is similar to other Cr^{III}-Cl bonds.[10]

Treatment of **1^b** with a Ti^{IV} titanatrane, **3** in tetrahydrofuran, synthesized according to the method of Verkade and coworkers,[13] afforded heterobimetallic **4^b** in high yield (75%) as a burnt orange powder. The high-spin Cr^{III} center was maintained ($\mu_{eff} = 3.10\ \mu_{BM}$). Vapor diffusion of *n*-pentane into a dichloromethane solution afforded burnt-orange crystals of **4^b** suitable for diffraction.

The structural parameters around the chromium ion show only small changes upon formation of the heterobimetallic complex. The Cr1-O1 bond length of **4^b** slightly decreases to 1.850(2) Å compared to 1.874(2) Å in **1^b**. This shortening of the Cr1-O1 bond is similar to that observed by Roesky in Ti-O-Zr systems, where the heterobimetallic M-O bond lengths were shorter than the terminal hydroxide precursors.[14] This can be explained if Ti^{IV} has a negligible effect on the Lewis acidity of the Cr^{III} center.[15] Other Cr^{III}-ligand distances and angles in **4^b** remain nearly unchanged from **1^b**.

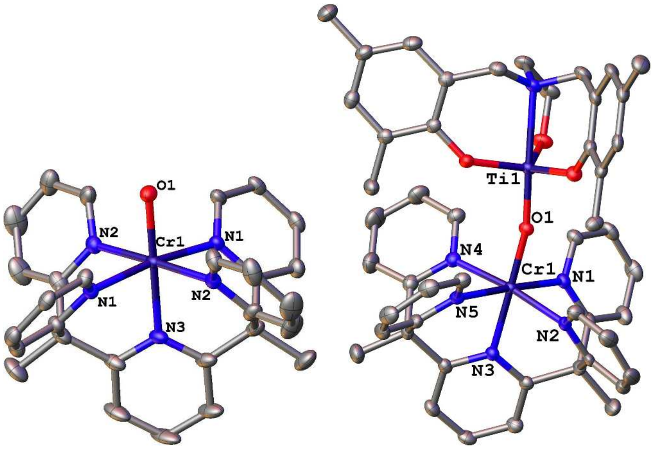


Figure 1 X-ray crystal structures of **1^b** (left) and **4^b** (right). Hydrogen atoms and BAr$_4$' anions have been omitted for clarity. Selected interatomic distances (Å): for 1^b: Cr1-O1 1.8735(16), Cr1-N3 2.0912(17). For 4: Cr1-O1 1.850(2), Cr1-N3 2.076(3), Ti1-O1 1.779(2). Selected interatomic angles (°): for 1: O1-Cr1-N3 180.0. For 4: Ti1-O1-Cr1 166.88(14).

The Ti-O bond length is shown to be 1.779(2) Å, indicative of a covalent bond between titanium and oxygen.[16] The resulting Ti-O-Cr bond angle is 166.9(2)°, which is consistent with the d^0 systems reported by Roesky.[14] The angle of the linkage appears to be dependent on the steric bulk of the complex, bending as far as the ligand environment will allow in both this and Roesky's systems.[2] All other bond angles and distances around titanium remain similar to the phenoxy bound compounds of Verkade and coworkers.[13]

Cyclic voltammetry of **1^b** in acetonitrile exhibits two reversible reductions, one at -1.45V *vs*. Fc/Fc$^+$ corresponding to the Cr^{III}-Cr^{II} couple, with the other at -1.94V *vs*. Fc/Fc$^+$ corresponding to the Cr^{II}-Cr^{I} couple. Bimetallic complex **4^b** also displays two reversible reduction peaks. The first of which occurs at -1.33V *vs*. Fc/Fc$^+$ corresponding to an anodic shift in the Cr^{III}-Cr^{II} wave. An anodic shift is also observed in the Cr^{II}-Cr^{I} reduction at -1.85V *vs*. Fc/Fc$^+$. This decrease in the reduction potential of the Cr^{III} centers is the result of electrostatic interactions with the Ti^{IV} center.

In order to elucidate the absorption spectral features of **4^b** (Figure 1A), the electronic absorption spectra of mononuclear **1^b** and **3** were recorded, and the sum of their spectra were overlayed with the heterobimetallic dimer, **4^b** (Figure 1A). The mathematical difference was determined as (**1^b** + **3**) - **4^b**, and is depicted in Figure 1B (See ESI for procedural information). The difference spectrum was fit with two Gaussians, centered at 4.32 and 3.98 eV. We assign the lower energy transition to the O-Cr^{III} LMCT, which is 0.68 eV higher in energy when compared to **1^b**. This is evident as the negative feature in Figure 1B at 3.30 eV. A new absorption feature for **4^b** is evident as the fitted red curve in Figure 1B, and is assigned to the Cr^{III}-O-Ti^{IV} to Cr^{IV}-O-Ti^{III} MMCT transition.[17,18]

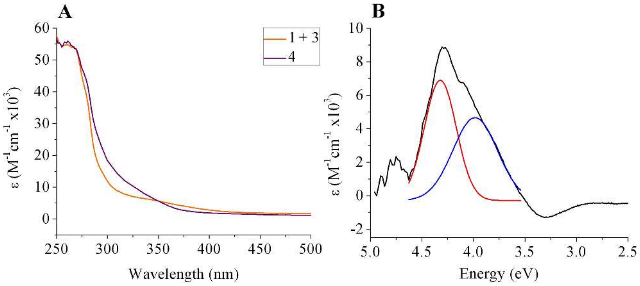


Figure 2 Combined absorption spectra of **1^b** and **3** (purple curve) versus **4^b** (orange curve) is depicted in A. The mathematical difference between the two curves results in the fitting of a new band at 4.32 eV (288 nm), assigned to the Cr^{III}-O-Ti^{IV} to Cr^{IV}-O-Ti^{III} MMCT (red curve) in B.

In summary, we have exploited the reactivity of an unsupported, terminal hydroxide to synthesize a heterobimetallic, *μ*-oxo bridged Cr^{III}-O-Ti^{IV} compound. To our knowledge, this is the first structurally characterized example of two different first row transition metal ions covalently bonded through an unsupported *μ*-oxo bridge. Heterobimetallic complex **4^b** exhibits a MMCT transition near 288 nm, and is the prototype of a new donor-acceptor architecture that may prove useful for solar energy conversion. Photophysical studies of this complex in addition to synthetic efforts to shift the MMCT transition to lower energies are currently underway.

Notes and references

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Electronic Supplementary Information (ESI) available: Complete synthetic details for all compounds, including EAS, and FT-IR. ^{1}H and ^{13}C NMR for **3**. Crystallographic information in CIF format for **1^b**, **2^b**, and **4^b**, CCSD 973877 (**4^b**), 973878 (**1^b**) and 983879 (**2^b**). See DOI: 10.1039/c000000x/

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