

## Mixed metal bis( $\mu$ -oxo) complexes with $[\text{CuM}(\mu\text{-O})_2]^{n+}$ ( $\text{M} = \text{Ni(III)}$ or $\text{Pd(II)}$ ) cores<sup>†</sup>

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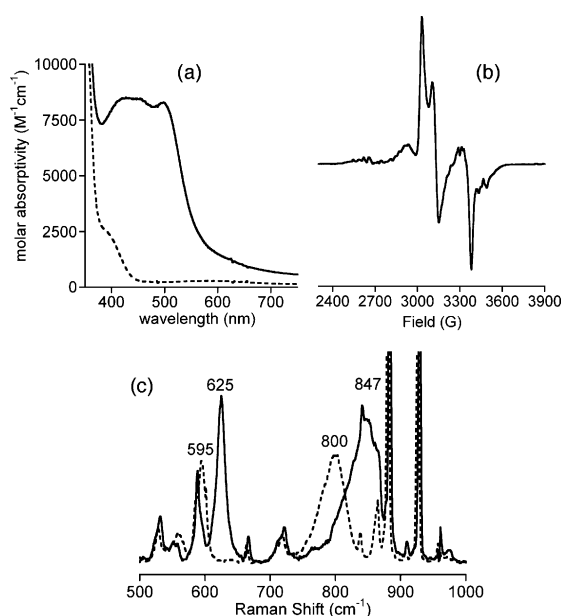
Two highly reactive heterodinuclear bis( $\mu$ -oxo) complexes were prepared by combining mononuclear peroxy species with reduced metal precursors at  $-80\text{ }^\circ\text{C}$  and were identified by UV-vis, EPR/NMR, and resonance Raman spectroscopy, with corroboration in the case of the CuPd system from density functional calculations.

The characterization of reactive metal–oxygen intermediates is an important objective in research aimed at understanding the mechanisms of oxidation catalysis in synthetic and biological systems.<sup>1</sup> As part of such efforts, bis( $\mu$ -oxo)dimetal complexes<sup>2</sup> of Cu,<sup>2,3</sup> Fe,<sup>2,4</sup> Co,<sup>5</sup> Ni,<sup>5–7</sup> and Pt<sup>8</sup> have been prepared, characterized, and shown in many instances to exhibit interesting oxidative reactivity. The syntheses of these compounds generally involve the reaction of an oxidant (e.g.,  $\text{O}_2$  or  $\text{H}_2\text{O}_2$ ) with mononuclear or homodinuclear precursors, and inevitably lead to complexes comprising  $[\text{M}_2(\mu\text{-O})_2]^{n+}$  or isomeric  $[\text{M}_2(\text{O}_2)]^{n+}$  cores with identical metal ions (M). Mixed-metal species  $[\text{MM}'(\mu\text{-O})_2]^{n+}$  are also of significant interest due to their potentially unique properties and their possible involvement in various catalytic processes,<sup>9,10</sup> yet they are exceedingly rare,<sup>11</sup> arguably because of intrinsic challenges associated with their preparation by the methods usually used to obtain symmetric  $[\text{M}_2\text{O}_2]^{n+}$  complexes. Bis( $\mu$ -oxo)dicopper complexes asymmetric by virtue of divergent N-donor supporting ligands on each metal were recently obtained by reacting a solution of a monocopper–peroxide complex (**1**)<sup>12</sup> with various LCu(I) compounds in the absence of free  $\text{O}_2$ .<sup>13,14</sup> Herein, we report the use of this type of sequential building block methodology to prepare novel complexes with  $[\text{CuNi}(\mu\text{-O})_2]^{2+}$  and  $[\text{CuPd}(\mu\text{-O})_2]^{1+}$  cores, thus demonstrating the applicability of a more general strategy for the preparation of heterodinuclear bis( $\mu$ -oxo) species.<sup>15</sup>

Addition of yellow  $[\text{PhTt}^{\text{tBu}}\text{Ni}(\text{CO})$  (**2**,  $\text{PhTt}^{\text{tBu}}$  = phenyltris(*tert*-butylthio)methyl)borate, a compound previously shown to react with  $\text{O}_2$  to yield a bis( $\mu$ -oxo)dinickel(III) complex,<sup>6</sup> to an anaerobic (purged with Ar) solution of green **1** in THF at  $-80\text{ }^\circ\text{C}$  resulted in the gradual formation ( $t_{1/2} \sim 4.5\text{ h}$ ,  $[\mathbf{1}] = [\mathbf{2}] = 0.7\text{ mM}$ ) of a deep red color and a broad, intense, and multifaceted absorption in the 400–600 nm region (Fig. 1a). This absorption bleaches upon warming to ambient temperature.<sup>‡</sup> The resonance Raman spectrum of the initial red solution ( $\lambda = 457.9\text{ nm}$ , frozen THF) contains peaks at 847 and 625  $\text{cm}^{-1}$  that shift to 800 and 595  $\text{cm}^{-1}$ , respectively, when **1** prepared with  $^{18}\text{O}_2$  was used (Fig. 1c). A (1,2-peroxy)dimetal complex is implicated by the 847/800 features ( $\nu_{\text{O-O}}$ ),<sup>§16</sup> which are inconsistent with monomeric 1 : 1 M/ $\text{O}_2$  species ( $\text{M} = \text{Cu}^{12}$  or  $\text{Ni}^{14}$ ). The 625/595 peaks are signatures of a bis( $\mu$ -oxo)dimetal core (symmetric  $\text{MM}'\text{O}_2$  vibration).<sup>2,17</sup> Importantly, the latter peak positions differ from those due to  $[(\text{PhTt}^{\text{tBu}}\text{Ni})_2(\mu\text{-O})_2]$  (590/560  $\text{cm}^{-1}$ ), thus supporting their attribution to a new mixed metal  $[\text{CuNi}(\mu\text{-O})_2]^{2+}$  core (**3**).<sup>¶</sup> The relative peak intensities suggest that the peroxy species is the major reaction

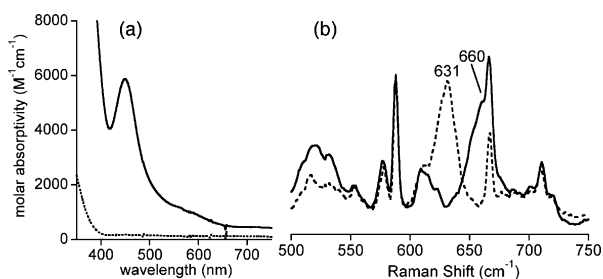
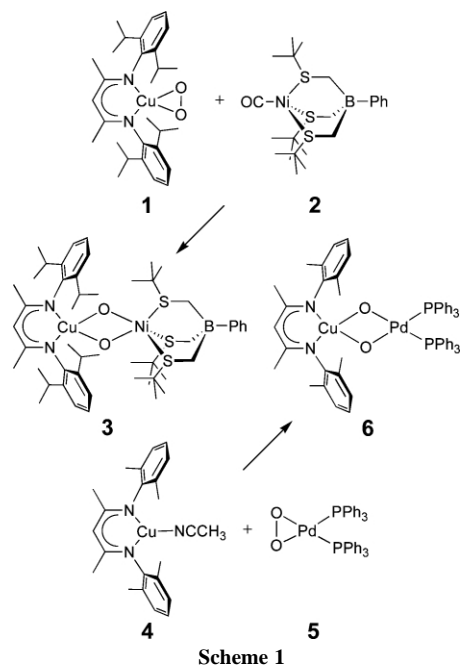
product, but selective decomposition of the bis( $\mu$ -oxo) Raman feature in the laser beam was observed, thus precluding attainment of an excitation profile and rendering the use of these intensities ineffective for assessing the product ratio. Indeed, the X-band EPR spectrum of the red solution (9.6 GHz, 2K) is dominated by a rhombic signal (Fig. 1b, apparent  $g_x = 2.03$ ,  $g_y = 2.19$ , and  $g_z = 2.26$ ) that lacks hyperfine splitting characteristic of Cu(II) ( $I = 3/2$ ), is a clear indicator of the presence of  $S = 1/2$  Ni(III), and corresponds by integration to  $\sim 90\%$  of the amount of **2** added.<sup>||</sup> The combined data thus indicate that bis( $\mu$ -oxo)copper(III)nickel(III) complex **3** is the primary reaction product, with a 1,2-peroxy species being a minor component despite the Raman data, which are deceptive due to the laser-induced decay of **3**. The peroxy species may be a precursor to **3**, but this notion has yet to be confirmed.

Using a complementary strategy to that implemented to prepare the CuNi compound **3**, the known<sup>18</sup> complex **5** (which we characterized by X-ray diffraction<sup>\*\*</sup>) was treated with the Cu(I) compound **4**<sup>19</sup> in THF at  $-80\text{ }^\circ\text{C}$ . A dark yellow-brown color and a new absorption band at  $\lambda_{\text{max}} = 448\text{ nm}$  ( $\epsilon 5900\text{ M}^{-1}\text{cm}^{-1}$ , Fig. 2a) developed immediately, which bleached upon warming. A spectrophotometric titration revealed that the maximum absorbance is attained when the molar ratio of **4** and **5** is 1 : 1. The product is EPR silent at 2K and exhibits a sharp  $^1\text{H}$  NMR spectrum (Fig. S4<sup>†</sup>) and a single peak in the  $^{31}\text{P}\{^1\text{H}\}$  spectrum (26.8 ppm, THF,  $-80\text{ }^\circ\text{C}$ ) distinct from that exhibited by **5** (34.2 ppm) and a decomposition product generated upon warming,  $\text{O=PPh}_3$  (24.7 ppm). Finally,



**Fig. 1** (a) Optical absorption spectra of a THF solution of **1** (dotted line) and the product of addition of equimolar **2** (solid line). (b) EPR spectrum of THF solution of **1** + **2** (1 mM, 9.6 GHz, 2K). (c) Resonance Raman spectrum of THF solution of  $\mathbf{1}\text{-}^{16}\text{O}_2 + \mathbf{2}$  (solid line) and  $\mathbf{1}\text{-}^{18}\text{O}_2 + \mathbf{2}$  (dotted line).

<sup>†</sup> Electronic supplementary information (ESI) available: experimental and calculation details. See <http://www.rsc.org/suppdata/cc/b4/b404640/>



**Fig. 2** (a) Optical absorption spectra of a THF solution of **5** (dotted line) and the product of addition of equimolar **4** (solid line). (b) Resonance Raman spectrum of THF solution of **5**- $^{16}\text{O}_2$  + **4** (solid line) and **5**- $^{18}\text{O}_2$  + **4** (dotted line).

excitation at  $\lambda = 457.9$  nm led to resonance enhancement of a peak at  $660\text{ cm}^{-1}$  in the Raman spectrum that shifted to  $631\text{ cm}^{-1}$  when **5** prepared with  $^{18}\text{O}_2$  was used (Fig. 2b). On the basis of the combined data, we postulate that the reaction of **4** with **5** produces the diamagnetic bis( $\mu$ -oxo)copper(III)palladium(II) complex **6**. Notably diagnostic for this formulation are the charge transfer transition at  $\lambda_{\text{max}} = 448$  nm and a  $\text{MM}'(\mu\text{-O})_2$  feature in the resonance Raman spectrum.<sup>2,17</sup> Further corroboration was provided by DFT calculations on **6**,<sup>†</sup> which yielded as an energy minimum a  $\text{C}_2$  structure with parameters typical for bis( $\mu$ -oxo)dimetal complexes (e.g.,  $\text{Cu-O} = 1.848\text{ \AA}$ ,  $\text{Pd-O} = 2.029\text{ \AA}$ ,  $\text{Pd}\cdots\text{Cu} = 2.994\text{ \AA}$ ) and a frequency for a  $\text{CuPd}(\mu\text{-O})_2$  rhomb mode of  $594\text{ cm}^{-1}$  ( $\Delta^{18}\text{O} = 26\text{ cm}^{-1}$ ). The isotope shift is in good agreement with the experimentally observed value, although the predicted frequency is somewhat low. Further theoretical work on **6** is underway.

In sum, we have successfully prepared heterodinuclear bis( $\mu$ -oxo) complexes by combining mononuclear peroxo species with reduced metal precursors. Both the CuNi and CuPd compounds are highly reactive, as shown by their tendency to decompose rapidly upon warming. Studies of their reactivity with exogenous substrates are underway, as are extensions of the synthetic methodology to other heterometal combinations.

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## Notes and references

<sup>†</sup> Reliable spectrophotometric titration data with which to confirm a 1 : 1 reaction stoichiometry were unavailable because of the slow rate of reaction at  $-80\text{ }^\circ\text{C}$  and competing decomposition at higher temperatures.

§ The value  $\Delta_{\text{obs}}(^{16}\text{O}-^{18}\text{O}) = 47\text{ cm}^{-1}$  closely matches  $\Delta_{\text{calc}}(^{16}\text{O}-^{18}\text{O}) = 49\text{ cm}^{-1}$  for a O–O harmonic oscillator.

¶ Oxygenation of the Cu(I) precursor of **1** does not yield a  $[\text{Cu}_2(\mu\text{-O})_2]^{2+}$  complex, thus arguing against the possibility that the  $625/595\text{ cm}^{-1}$  features are due to such a complex (which would also be diamagnetic and thus EPR silent).

|| EPR spectra recorded over a range of temperatures (2–65 K), microwave powers ( $5.0 \times 10^{-5}$ – $0.8\text{ mW}$ ), and reaction times (31–90 min.) contained the same features as shown in Fig. 1b. The small low field feature adjacent to the major rhombic signal is associated with the product of sample decomposition (supporting information<sup>†</sup>).

\*\* X-ray data for **5**- $^{16}\text{O}_2$ :  $\text{C}_{46.50}\text{H}_{42}\text{O}_2\text{P}_2\text{Pd}$ , MW =  $801.14\text{ g mol}^{-1}$ , monoclinic,  $a = 9.2639(14)$ ,  $b = 23.168(4)$ ,  $c = 18.260(3)\text{ \AA}$ ,  $\beta = 92.962(3)^\circ$ ,  $V = 3913.9(11)\text{ \AA}^3$ ,  $T = 173(2)\text{ K}$ ,  $P2(1)/n$ ,  $Z = 4$ ,  $\mu = 0.593\text{ mm}^{-1}$ , 25447 reflections, 6916 independent reflections [ $R(\text{int}) = 0.0562$ ],  $R1 = 0.0368$ ,  $wR2$  (for  $I > 2\sigma(I)$ ) =  $0.0831$ , 484 parameters, 43 restraints. CCDC 235181. See <http://www.rsc.org/suppdata/cc/b4/b404640d/> for crystallographic data in .cif or other electronic format.

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