

## SUPPORTING INFORMATION

### FOR

**Synthesis and Structural Characterization of Bi- and Trimetallic Octacyano-metalate(IV) Complexes:**  $[\Delta, \Lambda\text{-M}^{\text{II}}(\text{en})_3][\text{cis-M}^{\text{II}}(\text{en})_2(\text{OH}_2)][\text{M}^{\text{IV}}(\text{CN})_8] \cdot n\text{H}_2\text{O}$  and  $[\text{cis-M}^{\text{II}}(\text{en})_2(\text{OH}_2)]_2[(\mu\text{-NC})_2\text{M}^{\text{IV}}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mn, Co, Ni}$ ;  $\text{M}^{\text{IV}} = \text{Mo, W}$ ).

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Partial X-ray Structure of

$[\Lambda\text{-Mn}^{\text{II}}(\text{en})_3][\text{cis-Mn}^{\text{II}}(\text{en})_2(\text{OH}_2)(\mu\text{-NC})\text{W}^{\text{IV}}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$  (**2**).....S1

Distorted square antiprismatic  $\text{W}^{\text{IV}}(\text{CN})_8^{4-}$  center in **2**.....S2

X-ray Structure of

$[\Delta\text{-Ni}^{\text{II}}(\text{en})_3][\text{cis-Ni}(\text{en})_2(\text{OH}_2)(\mu\text{-NC})\text{-Mo}^{\text{IV}}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$  (**5**).....S3

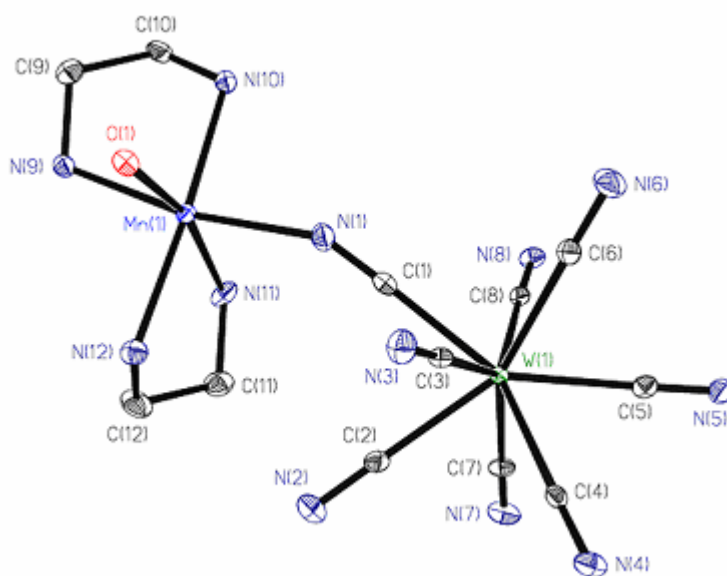
Partial X-ray Structure of

$[\Delta\text{-Ni}^{\text{II}}(\text{en})_3][\text{cis-Ni}^{\text{II}}(\text{en})_2(\text{OH}_2)(\mu\text{-NC})\text{W}^{\text{IV}}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$  (**6**).....S4

X-ray Structure of

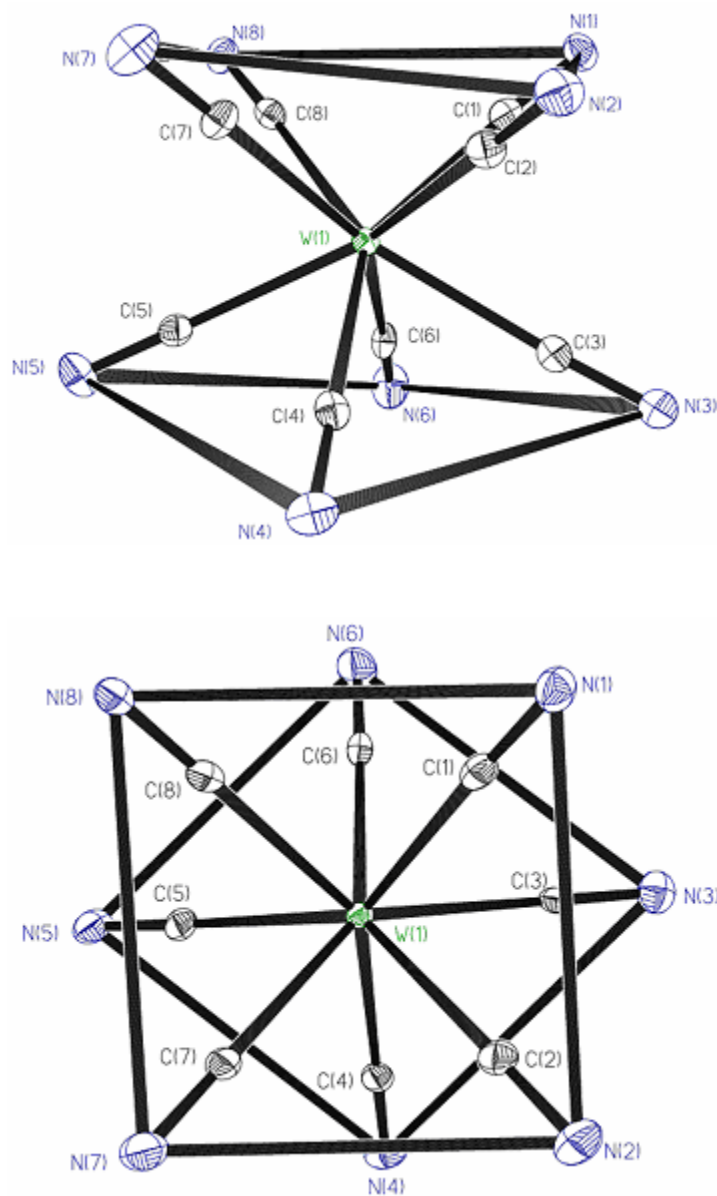
$[\Delta\text{-Ni}^{\text{II}}(\text{en})_3][\text{cis-Ni}^{\text{II}}(\text{en})_2(\text{OH}_2)(\mu\text{-NC})\text{W}^{\text{IV}}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$  (**6**).....S5

X-ray structure of  $[\text{cis-Ni}(\text{en})_2(\text{OH}_2)]_2[(\mu\text{-NC})_2\text{Mo}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$  (**7**).....S6



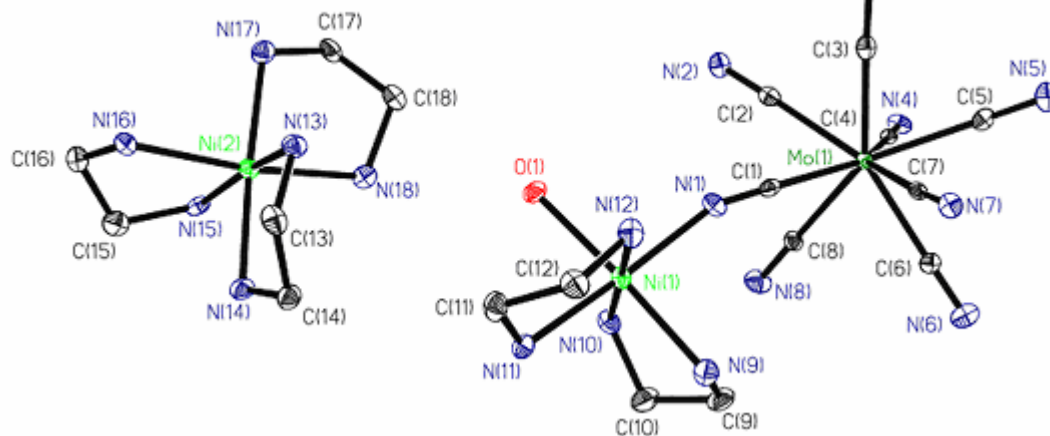
**Figure S1.** Partial X-ray Structure of [ $\Lambda$ -Mn<sup>II</sup>(en)<sub>3</sub>][*cis*-Mn<sup>II</sup>(en)<sub>2</sub>(OH<sub>2</sub>)( $\mu$ -NC)-W<sup>IV</sup>(CN)<sub>7</sub>] $\cdot$ 2H<sub>2</sub>O (**2**). Ellipsoids are at the 50% probability level and hydrogen atoms are eliminated for clarity. Only water oxygen (red), nitrogen (blue), carbon (black), tungsten (green), and manganese (blue) are illustrated.

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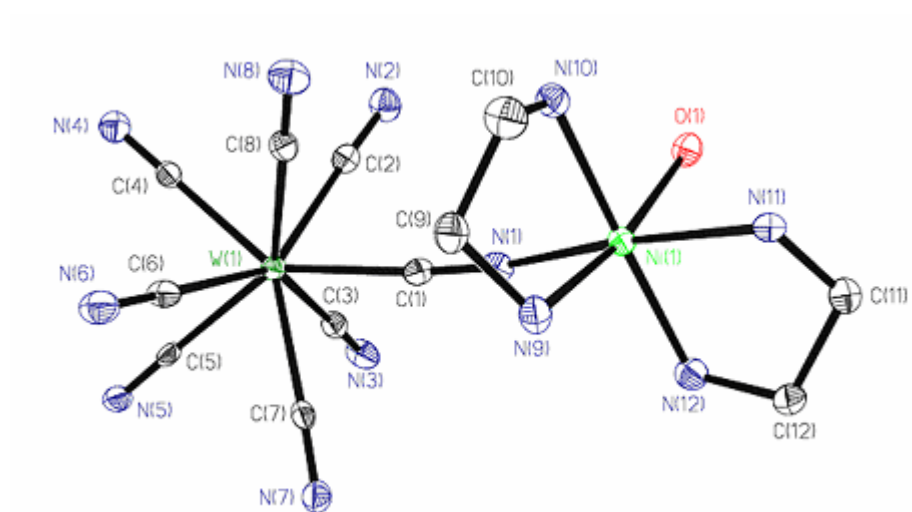
**Figure S2.** Distorted square antiprismatic  $W^{IV}(CN)_8^{4-}$  center in **2**. Ellipsoids are at the 50 % level.

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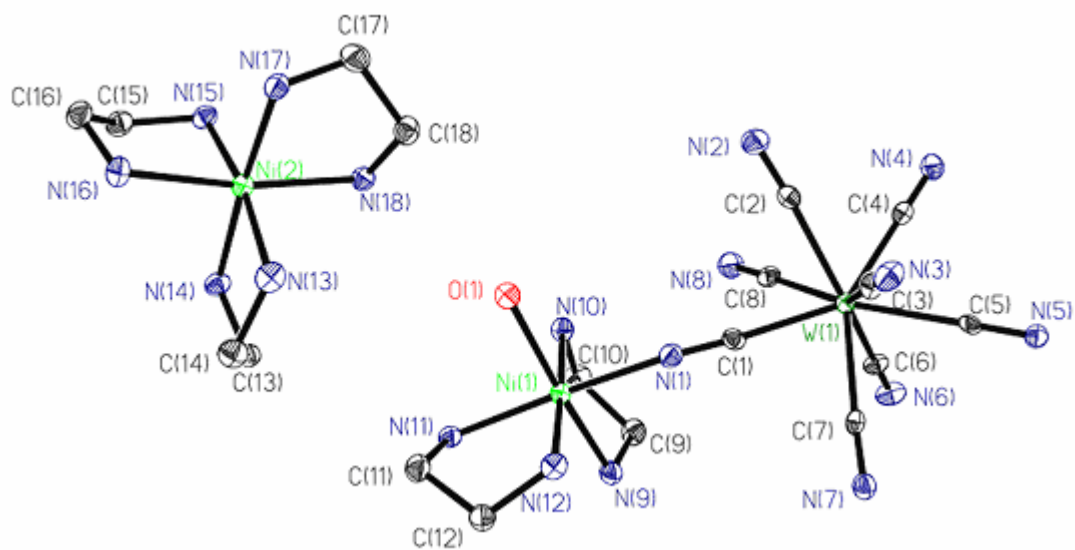
**Figure S3.** X-ray Structure of  $[\Delta\text{-Ni}^{\text{II}}(\text{en})_3][\text{cis-Ni}(\text{en})_2(\text{OH}_2)(\mu\text{-NC})\text{-Mo}^{\text{IV}}(\text{CN})_7]\cdot 2\text{H}_2\text{O}$  (**5**). Ellipsoids are at the 50% probability level and all hydrogen atoms are eliminated for clarity. Only water oxygen (red), nitrogen (blue) carbon (black), molybdenum (green), and nickel (lime green) are illustrated.

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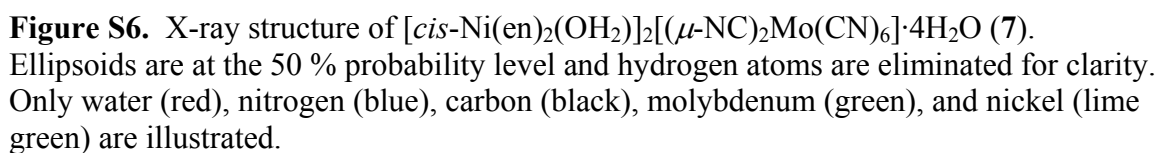
**Figure S4.** Partial X-ray Structure of  $[\Delta\text{-Ni}^{\text{II}}(\text{en})_3][\text{cis-Ni}^{\text{II}}(\text{en})_2(\text{OH}_2)(\mu\text{-NC})\text{-W}^{\text{IV}}(\text{CN})_7]\cdot 2\text{H}_2\text{O}$  (**6**). Hydrogen atoms and  $[\Delta\text{-Ni}^{\text{II}}(\text{en})_3]$  cations are eliminated for clarity and ellipsoids are at the 50% probability level. Only water oxygen (red), nitrogen (blue) carbon (black), tungsten (green), and nickel (lime green) are illustrated.

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**Figure S5.** X-ray Structure of  $[\Delta\text{-Ni}^{\text{II}}(\text{en})_3][\text{cis-Ni}^{\text{II}}(\text{en})_2(\text{OH}_2)(\mu\text{-NC})\text{W}^{\text{IV}}(\text{CN})_7]\cdot 2\text{H}_2\text{O}$  (**6**). Ellipsoids are at the 50% probability level and hydrogen atoms are eliminated for clarity. Only water oxygen (red), nitrogen (blue), carbon (black), tungsten (green), and nickel (lime green) are illustrated.

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