Electronic supplementary information

Heterometallic Re/Mo and Re/W cubane-type cluster complexes

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<table>
<thead>
<tr>
<th>Identification code</th>
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<tr>
<td>Empirical formula</td>
<td>C₁₂K₆Mo₃N₁₂O₁₀ReSe₄</td>
<td>C₁₄H₂₆K₆Mo₃N₁₂O₁₀ReSe₄</td>
<td>C₁₂K₆N₁₂O₁₀Re₂Se₄W₂</td>
<td>C₁₃H₃Cs₆N₁₂O₁₆ReSe₄W₃</td>
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<td>Formula weight</td>
<td>1607.08</td>
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<td>Temperature/K</td>
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<td>Crystal system</td>
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<td>trigonal</td>
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<td>Space group</td>
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<td>Pnma</td>
<td>P3</td>
<td>P2₁/n</td>
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<td>a/Å</td>
<td>33.127(3)</td>
<td>11.8651(2)</td>
<td>33.1303(10)</td>
<td>18.6439(3)</td>
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<td>b/Å</td>
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<td>c/Å</td>
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<td>15.7889(3)</td>
<td>9.3359(5)</td>
<td>22.0131(4)</td>
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<td>β/°</td>
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<td>90</td>
<td>90</td>
<td>108.4950(10)</td>
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<td>Volume/Å³</td>
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<td>3973.02(13)</td>
<td>8874.4(7)</td>
<td>4052.83(13)</td>
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<td>Z</td>
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<td>4</td>
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<td>4</td>
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<td>ρcalc/g/cm³</td>
<td>2.674</td>
<td>2.619</td>
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<td>μ/mm⁻¹</td>
<td>11.151</td>
<td>8.446</td>
<td>16.313</td>
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<td>F(000)</td>
<td>6484.0</td>
<td>2897.0</td>
<td>7057.0</td>
<td>3911.0</td>
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<td>Crystal size/mm³</td>
<td>0.25 × 0.08 × 0.05</td>
<td>0.1 × 0.08 × 0.05</td>
<td>0.15 × 0.04 × 0.04</td>
<td>0.3 × 0.08 × 0.08</td>
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<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
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<td>2θ range for data collection/°</td>
<td>2.84 to 48.812</td>
<td>4.704 to 61.024</td>
<td>2.458 to 51.38</td>
<td>3.458 to 57.392</td>
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<td>Index ranges</td>
<td>-38 ≤ h ≤ 32, -16 ≤ h ≤ 14, -38 ≤ h ≤ 40, -21 ≤ h ≤ 25,</td>
<td>-35 ≤ k ≤ 25, -30 ≤ k ≤ 30, -40 ≤ k ≤ 40, -14 ≤ k ≤ 14,</td>
<td>-10 ≤ l ≤ 22, -20 ≤ l ≤ 22, -11 ≤ l ≤ 11, -29 ≤ l ≤ 29</td>
<td>-21 ≤ h ≤ 25, -14 ≤ k ≤ 14, -29 ≤ l ≤ 29</td>
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<tr>
<td>Reflections collected</td>
<td>34885</td>
<td>54820</td>
<td>159689</td>
<td>64300</td>
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<td>Independent reflections</td>
<td>15373 [Rint = 0.0641, Rsigma = 0.0939]</td>
<td>6215 [Rint = 0.0549, Rsigma = 0.0291]</td>
<td>22473 [Rint = 0.0705, Rsigma = 0.0410]</td>
<td>10457 [Rint = 0.0568, Rsigma = 0.0397]</td>
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<td>Data/restraints/parameters</td>
<td>15373/546/1162</td>
<td>6215/3/254</td>
<td>22473/154/1289</td>
<td>10457/26/456</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.022</td>
<td>1.181</td>
<td>1.106</td>
<td>1.148</td>
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<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
<td>R₁ = 0.0518, wR₂ = 0.0957</td>
<td>R₁ = 0.0420, wR₂ = 0.0863</td>
<td>R₁ = 0.0329, wR₂ = 0.0649</td>
<td>R₁ = 0.0314, wR₂ = 0.0752</td>
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<td>Final R indexes [all data]</td>
<td>R₁ = 0.0732, wR₂ = 0.1051</td>
<td>R₁ = 0.0478, wR₂ = 0.0883</td>
<td>R₁ = 0.0359, wR₂ = 0.0661</td>
<td>R₁ = 0.0326, wR₂ = 0.0758</td>
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<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>2.35/-1.14</td>
<td>1.52/-1.33</td>
<td>2.60/-1.73</td>
<td>1.95/-2.83</td>
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<td>Flack parameter</td>
<td>0.55(2)</td>
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Figure S1. Experimental (top) vs calculated (bottom) powder diffraction pattern for compound 1.

Figure S2. Experimental (top) vs calculated (bottom) powder diffraction pattern for compound 2.
**Figure S3.** Experimental (top) vs calculated (bottom) powder diffraction pattern for compound 3.

**Figure S4.** Experimental (top) vs calculated (bottom) powder diffraction pattern for compound 4.
Figure S5. Observed (top) vs calculated (bottom) isotopic distribution peak sets correspond to the cluster anionic adducts for compound 1.

Figure S6. Observed (top) vs calculated (bottom) isotopic distribution peak sets correspond to the cluster anionic adducts for compound 3.
Figure S7. Observed (top) vs calculated (bottom) isotopic distribution peak sets correspond to the cluster anionic adducts for compound 4.

Figure S8. Dependence of M–M and M–Se mean bond lengths for \([\{M_xRe_{4-x}Se_4\}(CN)_{12}]^{n-}\) clusters.