Hexahalorhenate(IV) salts of metal oxazolidine nitroxides
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Table S1. Crystallographic data for 1a, 1b, 2a and 2a·150 K.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>1a</th>
<th>1b</th>
<th>2a</th>
<th>2a·150 K</th>
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<td>C₃₀H₃₂N₆O₄Cl₆FeRe</td>
<td>C₃₀H₃₂N₆O₄Br₆FeRe</td>
<td>C₃₄H₃₈N₈O₄Cl₆CoRe</td>
<td>C₃₈H₄₄N₁₀O₄Cl₆CoRe</td>
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<td>Mr</td>
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<td>1080.55</td>
<td>1162.66</td>
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<td>cryst. syst.</td>
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<td>triclinic</td>
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<td>space group</td>
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<td>P1̅</td>
<td>P1̅</td>
<td>P2₁/c</td>
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<td>13.5159(6)</td>
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<td>10.9775(2)</td>
<td>11.1140(4)</td>
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<td>c/Å</td>
<td>10.7890(4)</td>
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<td>11.5719(3)</td>
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<td>α/deg</td>
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<td>105.576(5)</td>
<td>80.2539(19)</td>
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<tr>
<td>β/deg</td>
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<td>101.890(5)</td>
<td>78.1007(19)</td>
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<td>V/Å³</td>
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<td>887.72(9)</td>
<td>991.53(4)</td>
<td>2210.29(18)</td>
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<td>120.01(10)</td>
<td>120.01(10)</td>
<td>149.94(13)</td>
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<td>1</td>
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<td>no. of restraints</td>
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<td>0</td>
<td>0</td>
<td>18</td>
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<td>final R1, wR2b (I &gt; 2σ(I))</td>
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<td>0.0222, 0.0453</td>
<td>0.0704, 0.1250</td>
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<td>0.77/-0.73</td>
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* Graphite monochromators. ¹ R1 = Σ | |Fo| - |Fc| | / Σ |Fo|, wR2 = {Σ[w(Fo²-FCO²²)]²}/Σ[w(Fo²)]¹/2.
Table S2. Crystallographic data for 2a·200 K, 2a·250 K and 2b.

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<td>C₃₈H₄₄N₁₀O₄Cl₆CoRe</td>
<td>C₃₀H₃₂N₆O₄Br₆CoRe</td>
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<td>space group</td>
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<td>P̅</td>
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<td>90</td>
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<td>2.20/-0.85</td>
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<td>1.31/-1.77</td>
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</table>

a Graphite monochromators. b \( R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \) and \( wR2 = \left( \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right)^{1/2}. \)
Table S3. Crystallographic data for 3a, 3b, 4a and 4b.

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<th>4b</th>
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<td>C_{60}H_{32}N_{6}O_{4}Br_{5}CuRe</td>
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<td>P̅1</td>
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<td>3927.4(3)</td>
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<td>120.01(10)</td>
<td>120.01(10)</td>
<td>120.01(10)</td>
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<td>final R1, wR2^{b} (l&gt;2α(l))</td>
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<td>0.0195, 0.0499</td>
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<td>0.97/-1.10</td>
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* Graphite monochromators. ^b R1 = Σ ||F_o|| - |F_c|| / Σ |F_o||, wR2 = {Σ[w(F_o^2-F_c^2)^2]/Σ[w(F_o^2)]}^{1/2}. 
Table S4. Selected bond lengths (Å) and angles (°) for 1a, 1b, 2a, 2a·150 K, 2a·200 K, 2a·250 K.

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<th>1b (M = Fe)</th>
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### Table S6. Selected bond lengths (Å) and angles (°) for 3a and 3b.

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Table S7. Selected bond lengths (Å) and angles (°) for 4a and 4b.

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Table S8. Intermolecular distances (Å) and angles (°) found in all complexes. CH···π angles (θ) are taken from angle between the plane of the ring and the C-H bond while CH···π distances (d) are from the carbon of the CH moiety to the centroid of the ring.

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Table S9. Selected bond lengths (Å) for 2a, 2a·150 K, 2a·200 K, 2a·250 K, 2b, [Co\(^{II}\)(L\(^{+}\))\(_2\)](NO\(_3\))\(_2\) (A), \(^{1}\)[Co\(^{III}\)(L\(^{-}\))\(_2\)](BPh\(_4\)) (B), \(^{1}\)[Co\(^{II}\)(L\(^{+}\))\(_2\)](B(C\(_6\)F\(_5\))\(_4\))\(_2\)·CH\(_2\)Cl\(_2\) (C)\(^{2}\) and [Co\(^{II}\)(L\(^{+}\))\(_2\)](B(C\(_6\)F\(_5\))\(_4\))\(_2\)·2Et\(_2\)O (D)\(^{2}\) at temperatures shown. Low-spin (LS), high spin (HS), neutral radical (L\(^{+}\)) and hydroxylamino anionic (L\(^{-}\)) assigned forms of the cobalt ion and the ligand are shown in the table below. See Fig. S1 for labelling of atoms.

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Table S10. Summary of selected octahedral nickel salts containing three coordinated acetonitrile solvate molecules. The loss of coordinated acetonitrile is based on the microanalysis of the relevant complex.

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<td>[Ni(L)(CH(_3)CN)](3)(ClO(_4))·0.5H(_2)O</td>
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<tr>
<td>[Tp(^{Pr})(^2)Ni(CH(_3)CN)](3)OTf</td>
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<td>11</td>
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<tr>
<td>[Tp(^{Ph})(^{Me})Ni(CH(_3)CN)](3)OTf</td>
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Abbreviations: pyS = 2-mercaptopyridinate; L\(^1\) = N\(_2\)O\(_2\)S\(_2\) macrocycle; Tpm\(^{Me,Me}\) = tris(3,5-dimethylpyrazol-1-yl)methane; Tpm\(^{Ph}\) = tris(3-phenylpyrazol-1-yl)methane; (Me-Tp)\(_2\)PMA = bis(5-methyl-2-thiophenemethyl)(2-pyridylmethyl)amine; P\(^{Bu}\)\(^2\)N\(^{Ph}\)\(^2\) and P\(^{Bu}\)\(^2\)N\(^{Bz}\)\(^2\) = cyclic diphosphine; L = 1,4,7-tris(cyanomethyl)-1,4,7-triazacyclononane; L\(^1\) = bis(1-methylbenzimidazolyl-2-methyl)amine; L\(^2\) = bis(1-methylbenzimidazolyl-2-methyl)-10-camphorsulfonamide; L\(^3\) = 1,3,5-tribenzyl-1,3,5-triazinane; L\(^4\) = 1,3,5-tris(2-fluorobenzyl)-1,3,5-triazinane; Tp\(^{R}\)\(^2\) = hydrotrispyrazolylborato with R group shown.
Figure S1. Labelled molecular structure of the [Co\(^{II}\)(L')\(_2\)]\(^{2+}\) (left) and [Ni\(^{II}\)(L')(MeCN)]\(^{2+}\) cations. The labelling shown for the [Co\(^{II}\)(L')\(_2\)]\(^{2+}\) cation (left) is representative of that employed in complexes 1a, 1b, 2a, 2b, 4a and 4b. The labelling shown for the [Ni\(^{II}\)(L')(MeCN)]\(^{2+}\) cation (right) is representative of that employed for 3a and 3b. Hydrogen atoms removed for clarity. Colour code: Co, light blue; Ni, cyan; N, blue; O, red; C, grey.
Figure S2. Infrared spectra of 3a(dried) and 3a(solvated). In 3a(solvated) the bands associated with both coordinated and solvated acetonitrile are clearly present (e.g. 2308, 2281 and 2253 cm\(^{-1}\)). For 3a(dried) the bands associated with acetonitrile disappear and bands associated with water absorption around 3400 cm\(^{-1}\) are observed.
Figure S3. Infrared spectra of 3b(dried) and 3b(solvated). In 3b(solvated) the bands associated with both coordinated and solvated acetonitrile are clearly present (e.g. 2316, 2289 and 2253 cm\(^{-1}\)). For 3b(dried) the bands associated with acetonitrile disappear and bands associated with water absorption around 3400 cm\(^{-1}\) are observed.
Figure S4. Intermolecular CH⋯π (top) and Cl⋯π (bottom) interactions for complex 1a. Selected hydrogens and disordered second part of oxazolidine ring hidden for clarity. Colour code: Re, dark blue; Fe, yellow; Cl, dark green; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.
**Figure S5.** Intermolecular CH⋯π (top) and Br⋯π (bottom) interactions for complex 1b. Selected hydrogens and disordered second part of oxazolidine ring hidden for clarity. Colour code: Re, dark blue; Fe, yellow; Br, dark red; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.
**Figure S6.** CH⋯π interactions for complex 2a. Selected hydrogens and acetonitrile solvate molecule removed for clarity. Colour code: Co, light blue; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.
Figure S7. Crystal structure of the [Co\textsuperscript{II}(L\textsuperscript{•})\textsubscript{2}]\textsuperscript{2+} cation at 150 (2a·150 K), 200 (2a·200 K) and 250 K (2a·250 K)) with bond lengths (Å) indicated. Hydrogen atoms omitted for clarity. Colour code: Co, dark blue; N, blue; O, red; C, grey. Hydrogen atoms omitted for clarity.
Figure S8. Crystal packing diagram of 2a-150 K as viewed down the b-axis. This packing is representative of the packing present in 2a-200 K and 2a-250 K. Hydrogens atom and solvate acetonitrile molecules hidden for clarity. Colour code: Re, dark blue; Co, light blue; Cl, dark green; N, blue; O, red; C, grey.
**Figure S9.** Intermolecular CH···π (top) and Br···π (bottom) interactions for complex 2b. Selected hydrogens hidden for clarity. Colour code: Re, dark blue; Co, light blue; Br, dark red; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.
**Figure S10.** CH···π interactions for complex 3a. Selected hydrogens and acetonitrile solvate molecule removed for clarity. Colour code: Ni, cyan; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.
Figure S11. Intermolecular CH···π (top) and Br···Br interactions (bottom) for complex 3b. Selected hydrogens hidden for clarity. Colour code: Ni, cyan; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.
Figure S12. Intermolecular CH···π (top) and Cl···π (bottom) interactions for complex 4a. Selected hydrogens and disordered second part of oxazolidine ring hidden for clarity. Colour code: Re, dark blue; Cu, green; Cl, dark green; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.
Figure S13. Intermolecular CH···π (top) and Br···π (bottom) interactions for complex 4b. Selected hydrogens hidden for clarity. Colour code: Re, dark blue; Cu, green; Br, dark red; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.
Figure S14. The $\chi_M$ vs $T$ plot for complex 1a and 1b.
Figure S15. The $\chi_M$ vs T plot for complex 2a and 2b.
Figure S16. Powder X-ray diffraction (PXRD) experiments on 3a(dried) (top left), 3b(dried) (top right), 3a(solvated) (bottom left) and 3b(solvated) (bottom right) were performed on a Rigaku Oxford Diffraction SuperNova X-ray diffractometer at 298 K with a scan step size of 0.086° at a rate of 1° sec⁻¹. Calculated patterns from single crystal data were made using Mercury 3.7.
Figure S17. The $\chi_M$ vs $T$ plot for complex 3a and 3b, dried and solvated.
Figure S18. The $\chi_M$ vs $T$ plot for complex 4a and 4b.
References


