Supporting Information

Synthesis, structure and light scattering properties of tetraalkylammonium metal isothiocyanate salts.

Didier Savard and Daniel B. Leznoff

Table S1. Comparison of the infrared data for $(\text{Me}_4\text{N})_3[\text{Fe(NCS)}_6]$ (7), $(\text{Et}_4\text{N})_3[\text{Fe(NCS)}_6]$ (8) and $(\text{n-Bu}_4\text{N})_3[\text{Ln(NCS)}_6]$ (Ln = Eu(III) (11), Gd(III) (12) and Dy(III) (13)) with literature values for these salts.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Observed (cm$^{-1}$)</th>
<th>Published</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>2073, 2058, 2023</td>
<td>2075, 2057, 2026</td>
<td>A</td>
</tr>
<tr>
<td>8</td>
<td>2101, 2070, 2054</td>
<td>2098, 2052</td>
<td>B</td>
</tr>
<tr>
<td>11</td>
<td>2047, 2037</td>
<td>2040</td>
<td>C</td>
</tr>
<tr>
<td>12</td>
<td>2043</td>
<td>2045</td>
<td>C</td>
</tr>
<tr>
<td>13</td>
<td>2054</td>
<td>2052</td>
<td>C</td>
</tr>
</tbody>
</table>

Table S2. Crystallographic data for (NH₄)₃[Cr(NCS)₆]·[(CH₃)₂CO] (1b), (Me₄N)₃[Cr(NCS)₆] (2), (Me₄N)₄[Mn(NCS)₆] (5), (Et₄N)₃[Mn(NCS)₅] (6) and (n-Bu₄N)₃[Fe(NCS)₆] (9).

<table>
<thead>
<tr>
<th>Complex</th>
<th>1b</th>
<th>2</th>
<th>5</th>
<th>6</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₉H₂₂CrN₁₀OS₆</td>
<td>C₁₈H₃₆CrN₉S₆</td>
<td>C₂₂H₴₆MnN₁₀S₆</td>
<td>C₂₉H₴₆MnN₁₈S₆</td>
<td>C₃₄H₁₀₈FeN₉O₀.₄₂S₆</td>
</tr>
<tr>
<td>Formula weight</td>
<td>530.73</td>
<td>622.94</td>
<td>700.01</td>
<td>736.11</td>
<td>1138.45</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293</td>
<td>293</td>
<td>293</td>
<td>293</td>
<td>293</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pcmn</td>
<td>C2/c</td>
<td>P2₁/n</td>
<td>P-1</td>
<td>Pa-3</td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.6828(16)</td>
<td>24.8961(10)</td>
<td>12.5278(6)</td>
<td>9.9359(9)</td>
<td>24.1615(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.744(2)</td>
<td>9.3234(4)</td>
<td>12.4262(6)</td>
<td>14.68914(1)</td>
<td>24.1615(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>16.341(3)</td>
<td>28.4594(12)</td>
<td>12.5900(6)</td>
<td>15.91915(1)</td>
<td>24.1615(2)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>80.442(16)</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
<td>90</td>
<td>100.021(2)</td>
<td>90.076(2)</td>
<td>72.682(17)</td>
<td>90</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>81.387(18)</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2332.9(7)</td>
<td>6505.1(5)</td>
<td>1959.92(16)</td>
<td>2175.4(4)</td>
<td>14105.0(2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>8</td>
<td>2</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>ρcalc (g/cm³)</td>
<td>1.511</td>
<td>1.272</td>
<td>1.186</td>
<td>1.124</td>
<td>1.072</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>1.049</td>
<td>6.680</td>
<td>0.683</td>
<td>0.571</td>
<td>0.429</td>
</tr>
<tr>
<td>R [Iᵣ ≥ 2.0σ(Iᵣ)]</td>
<td>0.0564</td>
<td>0.0521</td>
<td>0.0948</td>
<td>0.0709</td>
<td>0.0292</td>
</tr>
<tr>
<td>Rw [Iᵣ ≥ 2.0σ(Iᵣ)]</td>
<td>0.0562</td>
<td>0.0557</td>
<td>0.0910</td>
<td>0.0787</td>
<td>0.0322</td>
</tr>
</tbody>
</table>

Function minimized Σw(|Fᵣ| - |F_c|)² where w⁻¹ = σ²(Fᵣ) + 0.0002 Fᵣ², R = Σ|Fᵣ| - |F_c|/|ΣFᵣ|, R_w = (Σw(|Fᵣ| - |F_c|)²)/Σw|Fᵣ|²)¹/₂.
Table S3. Crystallographic data for (n-Bu$_4$N)$_3$[Ln(NCS)$_6$] (Ln = Eu(III) (11), Gd(III) (12) and Dy(III) (13)).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C$<em>{54}$H$</em>{108}$EuN$_9$S$_6$</td>
<td>C$<em>{54}$H$</em>{108}$GdN$_9$S$_6$</td>
<td>C$<em>{54}$H$</em>{108}$DyN$_9$S$_6$</td>
</tr>
<tr>
<td>formula weight</td>
<td>1227.87</td>
<td>1233.16</td>
<td>1238.41</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293</td>
<td>150</td>
<td>293</td>
</tr>
<tr>
<td>crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P-1</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>12.41400(10)</td>
<td>12.4039(16)</td>
<td>12.4126(3)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>12.88360(10)</td>
<td>12.8837(16)</td>
<td>12.8565(3)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>22.7811(2)</td>
<td>22.787(3)</td>
<td>22.7613(5)</td>
</tr>
<tr>
<td>$\alpha$ (deg)</td>
<td>90.9370(10)</td>
<td>90.877(6)</td>
<td>90.8850(10)</td>
</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>92.3400(10)</td>
<td>92.241(7)</td>
<td>92.3090(10)</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
<td>96.7250(10)</td>
<td>96.743(7)</td>
<td>96.6870(10)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>3614.63(5)</td>
<td>3612.8(8)</td>
<td>3603.93(14)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\rho_{calc}$ (g/cm$^3$)</td>
<td>1.127</td>
<td>1.171</td>
<td>1.141</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>1.077</td>
<td>1.165</td>
<td>1.246</td>
</tr>
<tr>
<td>$R$ [$I_o \geq 2.0\sigma(I_o)$]</td>
<td>0.0342</td>
<td>0.0520</td>
<td>0.0353</td>
</tr>
<tr>
<td>$R_w$ [$I_o \geq 2.0\sigma(I_o)$]</td>
<td>0.0360</td>
<td>0.0504</td>
<td>0.0324</td>
</tr>
</tbody>
</table>

Function minimized $\sum w(|F_o|-|F_c|)^2$ where $w^{-1} = \sigma^2(F_o) + 0.0002 F_o^2$.

Table S4. Selected bond lengths (Å) and angles (°) for (NH$_4$)$_3$[Cr(NCS)$_6$]·[(CH$_3$)$_2$CO] (1b), (n-Bu$_4$N)$_3$[Cr(NCS)$_6$] (4), (Me$_4$N)$_4$[Mn(NCS)$_6$] (5) and (n-Bu$_4$N)$_3$[Fe(NCS)$_6$] (9).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>1b</th>
<th>4</th>
<th>5</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-N1</td>
<td>2.005(5)</td>
<td>2.057(1)</td>
<td>2.202(9)</td>
<td>2.061(3)</td>
</tr>
<tr>
<td>M-N2</td>
<td>1.997(4)</td>
<td>2.026(1)</td>
<td>2.214(9)</td>
<td>2.032(3)</td>
</tr>
<tr>
<td>M-N3</td>
<td>1.992(4)</td>
<td>--</td>
<td>2.223(8)</td>
<td>--</td>
</tr>
<tr>
<td>M-N4</td>
<td>2.000(5)</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>M-N1-C</td>
<td>177.2(5)</td>
<td>168.23(1)</td>
<td>176.7(9)</td>
<td>168.8(3)</td>
</tr>
<tr>
<td>M-N2-C</td>
<td>170.1(4)</td>
<td>173.95(1)</td>
<td>176.9(9)</td>
<td>173.6(3)</td>
</tr>
<tr>
<td>M-N3-C</td>
<td>165.8(4)</td>
<td>--</td>
<td>169.5(9)</td>
<td>--</td>
</tr>
<tr>
<td>M-N4-C</td>
<td>168.1(5)</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
Table S5. Selected bond lengths (Å) and angles (°) for (Me₄N)₃[Cr(NCS)₆] (2).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr1-N1</td>
<td>1.999(5)</td>
<td></td>
</tr>
<tr>
<td>Cr1-N2</td>
<td>1.993(5)</td>
<td></td>
</tr>
<tr>
<td>Cr1-N3</td>
<td>1.992(5)</td>
<td></td>
</tr>
<tr>
<td>Cr2-N4</td>
<td>1.999(4)</td>
<td></td>
</tr>
<tr>
<td>Cr2-N5</td>
<td>1.993(5)</td>
<td></td>
</tr>
<tr>
<td>Cr2-N6</td>
<td>1.985(5)</td>
<td></td>
</tr>
<tr>
<td>Cr1-N1-C1</td>
<td>177.4(4)</td>
<td></td>
</tr>
<tr>
<td>Cr1-N2-C2</td>
<td>173.8(4)</td>
<td></td>
</tr>
<tr>
<td>Cr1-N3-C3</td>
<td>150.9(4)</td>
<td></td>
</tr>
<tr>
<td>Cr2-N4-C4</td>
<td>175.9(4)</td>
<td></td>
</tr>
<tr>
<td>Cr2-N5-C5</td>
<td>176.8(4)</td>
<td></td>
</tr>
<tr>
<td>Cr2-N6-C6</td>
<td>171.8(4)</td>
<td></td>
</tr>
</tbody>
</table>

Table S6. Selected bond lengths (Å) and angles (°) for (Et₄N)₃[Mn(NCS)₃] (6).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn1-N1</td>
<td>2.216(5)</td>
<td>Mn1-N1-C1</td>
</tr>
<tr>
<td>Mn1-N2</td>
<td>2.110(5)</td>
<td>Mn1-N2-C2</td>
</tr>
<tr>
<td>Mn1-N3</td>
<td>2.143(4)</td>
<td>Mn1-N3-C3</td>
</tr>
<tr>
<td>Mn1-N4</td>
<td>2.226(4)</td>
<td>Mn1-N4-C4</td>
</tr>
<tr>
<td>Mn1-N5</td>
<td>2.173(4)</td>
<td>Mn1-N5-C5</td>
</tr>
<tr>
<td>N1-Mn1-N2</td>
<td>98.3(2)</td>
<td>N2-Mn1-N3</td>
</tr>
<tr>
<td>N1-Mn1-N3</td>
<td>87.8(2)</td>
<td>N2-Mn1-N4</td>
</tr>
<tr>
<td>N1-Mn1-N4</td>
<td>170.3(2)</td>
<td>N2-Mn1-N5</td>
</tr>
<tr>
<td>N1-Mn1-N5</td>
<td>85.9(2)</td>
<td>N4-Mn1-N5</td>
</tr>
<tr>
<td>N3-Mn1-N4</td>
<td>91.5(2)</td>
<td>N3-Mn1-N5</td>
</tr>
</tbody>
</table>
Table S7. Selected bond lengths (Å) and angles (°) for (n-Bu₄N)₃[Ln(NCS)₆] (Ln = Eu(III) (11), Gd(III) (12) and Dy(III) (13)).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-N1</td>
<td>2.379(3)</td>
<td>2.390(4)</td>
<td>2.341(4)</td>
</tr>
<tr>
<td>M-N2</td>
<td>2.395(3)</td>
<td>2.395(4)</td>
<td>2.340(4)</td>
</tr>
<tr>
<td>M-N3</td>
<td>2.382(3)</td>
<td>2.398(4)</td>
<td>2.350(4)</td>
</tr>
<tr>
<td>M-N4</td>
<td>2.387(3)</td>
<td>2.365(4)</td>
<td>2.333(4)</td>
</tr>
<tr>
<td>M-N5</td>
<td>2.405(3)</td>
<td>2.376(4)</td>
<td>2.340(4)</td>
</tr>
<tr>
<td>M-N6</td>
<td>2.381(3)</td>
<td>2.396(4)</td>
<td>2.364(4)</td>
</tr>
<tr>
<td>M-N1-C</td>
<td>176.2(3)</td>
<td>171.3(4)</td>
<td>172.7(4)</td>
</tr>
<tr>
<td>M-N2-C</td>
<td>174.8(3)</td>
<td>173.9(4)</td>
<td>172.3(4)</td>
</tr>
<tr>
<td>M-N3-C</td>
<td>171.8(3)</td>
<td>175.3(4)</td>
<td>174.6(4)</td>
</tr>
<tr>
<td>M-N4-C</td>
<td>172.5(3)</td>
<td>175.6(4)</td>
<td>176.5(4)</td>
</tr>
<tr>
<td>M-N5-C</td>
<td>174.4(3)</td>
<td>170.7(4)</td>
<td>172.7(4)</td>
</tr>
<tr>
<td>M-N6-C</td>
<td>172.0(3)</td>
<td>174.5(4)</td>
<td>174.0(4)</td>
</tr>
</tbody>
</table>
Figure S1. Crystal structure of \((\text{Me}_4\text{N})_3[\text{Cr(NCS)}_6]\) (2). Thermal ellipsoids are drawn at 50% probability. Colour code: Purple (Cr), Blue (N), Yellow (S), Gray (C). Solvent molecules and hydrogen atoms have been removed for clarity.

Figure S2. Measured PXRD pattern (black), Pawley refinement (red) and difference pattern (blue) of \((\text{Et}_4\text{N})_3[\text{Cr(NCS)}_6]\) (3a).

Figure S3. Generated crystal structure of \((\text{Bu}_4\text{N})_3[\text{Cr(NCS)}_6]\) (4) from the Rietveld refinement. Color code: Purple (Cr), Blue (N), Yellow (S), Gray (C). Solvent molecules were removed for clarity.
Figure S4. Measured PXRD pattern (black), calculated Rietveld refinement (red) and difference pattern (blue) of (n-Bu₄N)₃[Cr(NCS)₆] (4).

Table S8. Rietveld refinement parameters for (n-Bu₄N)₃[Cr(NCS)₆] (4).

<table>
<thead>
<tr>
<th>System</th>
<th>Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>Pa-3</td>
</tr>
<tr>
<td>Scale</td>
<td>8.644e-008</td>
</tr>
<tr>
<td>Lattice parameter, α (Å)</td>
<td>24.442</td>
</tr>
<tr>
<td>Unit Cell Volume (Å³)</td>
<td>14615</td>
</tr>
<tr>
<td>Crystal density, calculated (g cm³)</td>
<td>1.638</td>
</tr>
<tr>
<td>Wt%-Rietveld</td>
<td>100</td>
</tr>
<tr>
<td>Rexp / Rexp ′</td>
<td>8.316 / 17.065</td>
</tr>
<tr>
<td>Rwp / Rwp ′</td>
<td>11.398 / 23.388</td>
</tr>
<tr>
<td>Rp / Rp ′</td>
<td>8.889 / 22.824</td>
</tr>
<tr>
<td>R_Bragg</td>
<td>1.2839</td>
</tr>
<tr>
<td>GoF</td>
<td>1.371</td>
</tr>
<tr>
<td>DW_d</td>
<td>1.594</td>
</tr>
</tbody>
</table>
**Figure S5.** Crystal structure of (Me$_4$N)$_4$[Mn(NCS)$_6$] (5). The thermal ellipsoids are drawn at 50% probability. Colour code: Pink (Mn), Blue (N), Yellow (S), Gray (C). Hydrogen atoms have been removed for clarity.

**Figure S6.** Measured PXRD pattern (black), Pawley refinement (red) and difference pattern (blue) of (Me$_4$N)$_4$[Mn(NCS)$_6$] (5).
**Figure S7.** Measured PXRD pattern (black), Pawley refinement (red) and difference pattern (blue) of (Et₄N)₃[Mn(NCS)₅] (6).

**Figure S8.** Crystal structure of (n-Bu₄N)₃[Fe(NCS)₆] (9). The thermal ellipsoids are drawn at 50% probability. Colour code: Green (Fe), Blue (N), Yellow (S), Gray (C). Solvent molecules and hydrogen atoms have been removed for clarity.
Figure S9. Crystal structure of (n-Bu₄N)₃[Eu(NCS)₆] (11) (left), (n-Bu₄N)₃[Gd(NCS)₆] (12) (middle) and (n-Bu₄N)₃[Dy(NCS)₆] (13) (right). The thermal ellipsoids are drawn at 50% probability. Colour code: Purple (Eu), Light blue (Gd), Turquoise (Dy), Blue (N), Yellow (S), Gray (C).

Table S9. Pawley refinement parameters for (Et₄N)₃[Cr(NCS)₆] (3a), (Me₄N)₄[Mn(NCS)₆] (5) and (Et₄N)₃[Mn(NCS)₆] (6).

<table>
<thead>
<tr>
<th>Compound</th>
<th>3b</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
<td>Cubic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Ia-3</td>
<td>P21/n</td>
<td>P-1</td>
</tr>
<tr>
<td>a (Å)</td>
<td>26.92321</td>
<td>12.48869</td>
<td>9.86260</td>
</tr>
<tr>
<td>b (Å)</td>
<td>26.92321</td>
<td>12.22627</td>
<td>14.52658</td>
</tr>
<tr>
<td>c (Å)</td>
<td>26.92321</td>
<td>12.62604</td>
<td>15.70293</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>80.34524</td>
</tr>
<tr>
<td>β (°)</td>
<td>90</td>
<td>90.29675</td>
<td>72.62981</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
<td>81.41553</td>
</tr>
<tr>
<td>Rexp / Rexp ′</td>
<td>0.754 / 5.964</td>
<td>0.702 / 5.574</td>
<td>0.501 / 1.024</td>
</tr>
<tr>
<td>Rwp / Rwp ′</td>
<td>1.076 / 8.504</td>
<td>0.556 / 4.421</td>
<td>0.632 / 1.291</td>
</tr>
<tr>
<td>Rp / Rp ′</td>
<td>0.727 / 10.738</td>
<td>0.343 / 4.648</td>
<td>0.335 / 0.918</td>
</tr>
<tr>
<td>GoF</td>
<td>1.426</td>
<td>0.793</td>
<td>1.261</td>
</tr>
<tr>
<td>DWₐ</td>
<td>0.128</td>
<td>0.453</td>
<td>0.791</td>
</tr>
</tbody>
</table>
Figure S10. The solid-state visible reflectance spectra of (Me₄N)₃[Fe(NCS)₆] (7) as powder (black) and crystals (red).

Table S10. List of restrained bond distances in 5, 11 and 13.

<table>
<thead>
<tr>
<th></th>
<th>5</th>
<th>11</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>N5-C8</td>
<td>C45-C46</td>
<td>C25-C26</td>
<td></td>
</tr>
<tr>
<td>N5-C9</td>
<td>C21-C22</td>
<td>C41-C42</td>
<td></td>
</tr>
<tr>
<td>N5-C10</td>
<td>C45-C55</td>
<td>C13-C14</td>
<td></td>
</tr>
<tr>
<td>N5-C11</td>
<td>C21-C56</td>
<td>C10-C9</td>
<td></td>
</tr>
<tr>
<td>N4-C4</td>
<td></td>
<td>C22-C21</td>
<td></td>
</tr>
<tr>
<td>N4-C5</td>
<td></td>
<td>C32-C33</td>
<td></td>
</tr>
</tbody>
</table>
**Figure S11.** The solution UV-visible absorbance spectra of 7 (black), 8 (red) and 9 (blue), illustrating the identical single absorbance band at 496 nm for all three complexes.

**Figure S12.** The solid-state visible reflectance spectra of (n-Bu₄N)₃[Cr(NCS)₆] (4) as crystals (red) and powder (black).