Electronic Supporting Information for

Probing a variation of the inverse-trans-influence in americium and lanthanide tribromide tris(tricyclohexylphosphine oxide) complexes

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**PHOTOGRAPHS OF AMERICIUM SYNTHESIS**

**Figure S1.** Photograph of AmBr₃(OPcy₃)₃ in ¹PrOH (left) and 9.0 mg of crystalline material (Right).

**Figure S2.** Photograph of AmBr₃(OPcy₃)₃ NMR sample in CDCl₃ (left), and additional photograph of isolated crystals (right).
Figure S3. Room temperature UV/vis/NIR spectra of LaBr$_3$(OPcy)$_3$ in MeOH (red trace), DCM (black trace) and in the solid state (purple trace, right axis) and a photograph of a typical crystal. Identifiable peaks labeled with their $\lambda_{\text{max}}$ and $\varepsilon$ values are labeled in their corresponding colors. No identifiable transitions occur past 500 nm and the spectra have been truncated for clarity.
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Figure S5. Room temperature UV/vis/NIR spectra of PrBr$_3$(OPcy)$_3$ in MeOH (black trace), DCM (red trace) and in the solid state (purple trace, right axis) inset of 400-650 nm region and a photograph of a typical crystal. Identifiable peaks labeled with their $\lambda_{\text{max}}$ and $\varepsilon$ values are labeled in their corresponding colors with excitation symmetry labels. No identifiable transitions occur past 650 nm and the spectra have been truncated for clarity.
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**MULTI NUCLEAR NMR SPECTROSCOPY**

**Figure S8.** $^1$H NMR spectrum of $\text{AmBr}_3(\text{OPcy}_3)_3$ in CDCl$_3$ at 295 K with expansion of 8 – 0 ppm region. Because the chemical identity of the peaks is unclear the peaks are not integrated.
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$^1$H NMR spectrum of $\text{PrBr}_3(\text{OPcy})_3$ at 298 K in MeOD-$d_4$. 

$H_2O$

$HCD_2OD$
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CD$_2$Cl$_2$
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THEORETICAL CALCULATIONS

Table S1. Bond distances (Å) of all-electron geometry optimizations of $\text{MBr}_3(\text{OPMe}_3)_3$ (M = Ce, Nd, Am) in gas phase at PBE/TZP level of theory.

| Bond    | Ce   | Nd   | Am   |
|---------|------|------|------|
| M – O1  | 2.406| 2.376| 2.366|
| M – O2  | 2.406| 2.389| 2.364|
| M – O3  | 2.431| 2.391| 2.411|
| M – Br1 | 2.881| 2.839| 2.866|
| M – Br2 | 2.917| 2.886| 2.856|
| M – Br3 | 2.994| 2.903| 2.857|
Table S2. QTAIM metrics derived from SR-CAS wave functions for MBr\textsubscript{3}(OPcy)\textsubscript{3} (M = Ce, Nd, Am) complexes. With the following definitions: ρ(r) – electron density, (eÅ\textsuperscript{−3}), δ(r) – delocalization indices, V(r) – potential energy density (kJmol\textsuperscript{−1}Å\textsuperscript{−3}), G(r) – kinetic energy density (kJmol\textsuperscript{−1}Å\textsuperscript{−3}), and H(r) – total energy density (kJmol\textsuperscript{−1}Å\textsuperscript{−3}). H(r)/ρ(r) represents a "normalized" energy density per electron (kJmol\textsuperscript{−1}).

|      | C  | N  | A  | e  | d  | m  | C  | N  | A  | e  | d  | m  | C  | N  | A  | e  | d  | m  | C  | N  | A  | e  | d  | m  |
|------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| M(1) | 0  | 0  | 0  | 0  | 3  | 3  | -5 | 8  | 5  | 0  | 0  | 0  | 0  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5  |
| Br(1)| 5  | 6  | 8  | 2  | 1  | 5  | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 |
| Br(2)| 1  | 4  | 9  | 0  | 7  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  |
| Br(3)| 8  | 5  | 5  | 9  | 3  | 9  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  |
| M(1) | 0  | 0  | 0  | 0  | 3  | 3  | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 |
| Br(4)| 1  | 4  | 9  | 0  | 7  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  |
| M(1) | 0  | 0  | 0  | 0  | 3  | 3  | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 | -5 |
| O(1) | 9  | 5  | 8  | 5  | 2  | 9  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  |
| O(2) | 0  | 2  | 7  | 0  | 5  | 4  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |
| M(1) | 4  | 4  | 4  | 2  | 2  | 3  | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 |
| O(2) | 7  | 8  | 6  | 2  | 6  | 7  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  |
| M(1) | 6  | 4  | 8  | 6  | 2  | 0  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  |
| M(1) | 0  | 0  | 0  | 0  | 0  | 0  | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 |

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Table S2 Continued.

|      | V(r)/G(r) | H(r) | H(r)/ρ(r) |
|------|-----------|------|-----------|
|      | Ce        | Nd   | A         | Ce  | Nd  | A  |
|      | e | d | m | e | d | m | e | d | m |
| M(1)-Br(1) | 1 | 1 | 1 | 50 | 52 | 77 | 97 | 95 | 72 |
| M(1)-Br(2) | 1 | 0 | 4 | 43 | 43 | 68 | 78 | 74 | 54 |
| M(1)-Br(3) | 9 | 9 | 2 | 9  | 9  | 4  | 9  | 9  | 4  |
| M(1)-O(1)  | 1 | 1 | 1 | 54 | 50 | 82 | 97 | 92 | 84 |
| M(1)-O(2)  | 5 | 4 | 4 | .4 | .9 | .5 | 7  | 3  | 8  |
| M(1)-O(3)  | 0 | 0 | 0 | .6 | .3 | .6 | 4.6| 1.1| 9.3|
Table S3. Molecular orbital (MO) composition of $\text{AmBr}_3(\text{OPMe}_3)_3$ for the following orbital populations: Am – 6$p$, 5$f$, 6$d$; O – 2$s$, 2$p$; Br – 4$s$, 4$p$; P – 3$s$, 3$p$. Percentages in bold represent the main contribution to the MO. Energies given are relative to the first O 2$s$ MO.

| E(eV) | Am 6$p$ | Am 5$f$ | Am 6$d$ | O 2$s$ | O 2$p$ | Br 4$s$ | Br 4$p$ | P 3$s$ | P 3$p$ |
|-------|---------|---------|---------|--------|--------|--------|--------|--------|--------|
| 0.0   | 14%     |         |         | 66%    |        |        |        | 8%     | 4%     |
| 0.1   | 6%      |         |         | 69%    | 3%     |        |        | 11%    | 5%     |
| 0.4   |         |         |         | 73%    | 3%     |        |        | 11%    | 5%     |
| 2.6   | 96%     |         |         |        |        | 4%     |        |        |        |
| 2.7   | 89%     |         |         |        |        | 1%     | 3%     | 2%     |        |
| 2.8   | 78%     |         |         |        |        | 5%     | 7%     | 5%     |        |
| 8.1   |         |         |         |        |        |        |        | 100%   |        |
| 8.3   |         |         |         |        |        |        |        | 100%   |        |
| 8.4   | 2%      |         |         |        |        |        |        | 97%    |        |
| 14.7  |         |         |         |        |        |        | 31%    |        |        |
| 14.8  |         |         |         |        |        |        | 42%    |        | 10%    |
| 15.4  |         |         |         |        |        |        | 5%     | 40%    | 5%     |
| 17.4  | 3%      |         |         |        |        |        |        | 64%    |        |
| 17.5  | 2%      |         |         |        |        |        |        | 68%    |        |
| 17.7  | 3%      |         |         |        |        |        |        | 61%    |        |
| 17.7  |         |         |         |        |        |        |        | 68%    |        |
| 17.8  |         |         |         |        |        |        |        | 66%    |        |
| 17.9  |         |         |         |        |        |        |        | 66%    |        |
| 18.9  | 4%      |         |         |        |        |        |        |        | 84%    |
| 19.5  | 3%      | 3%      |         |        |        |        |        |        | 87%    |
| 19.7  | 2%      | 3%      |         |        |        |        |        |        | 91%    |
| 19.8  | 6%      | 3%      |         |        |        |        |        |        | 88%    |
| 19.9  | 3%      |         |         |        |        |        |        |        | 93%    |
| 20.0  | 2%      |         |         |        |        |        |        |        | 92%    |
| 20.0  |         |         |         |        |        |        |        |        | 91%    |
| 20.0  |         |         |         |        |        |        |        |        | 92%    |
| 20.3  | 2%      |         |         |        |        |        |        |        | 97%    |
| 22.2  |         |         |         |        |        | 100%   |        |        |        |
| 22.3  | 95%     |         |         |        |        |        |        |        | 1%     |
| 22.3  |         |         |         |        |        | 100%   |        |        |        |
| 22.3  | 95%     |         |         |        |        |        |        |        | 1%     |
| 22.5  | 89%     |         |         |        |        |        |        |        | 4%     |
| 22.5  | 89%     |         |         |        |        |        |        |        | 6%     |
| 22.5  |         |         |         |        |        |        |        |        | 91%    |
Table S4. Molecular orbital (MO) composition of CeBr₃(OPMe₃)₃ for the following orbital populations: Ce – 5p, 4f, 5d; O – 2s, 2p; Br – 4s, 4p; P – 3s, 3p. Percentages in bold represent the main contribution to the MO. Energies given are relative to the first O 2s MO.

| E(eV) | Molecular orbital composition |
|-------|-----------------------------|
|       | Ce 5p | Ce 4f | Ce 5d | O 2s | O 2p | Br 4s | Br 4p | P 3s | P 3p |
| 0.0   | 2%    |       |       | 71%  | 4%   | 11%  | 6%   |      |      |
| 0.1   | 4%    |       |       | 72%  | 2%   | 10%  | 6%   |      |      |
| 0.3   |       |       |       | 72%  | 1%   |      | 12%  | 6%   |      |
| 4.6   |       |       |       | 68%  | 7%   |      |      | 9%   |      |
| 4.7   |       |       |       | 70%  | 4%   | 1%   |      | 7%   |      |
| 4.8   |       |       |       | 93%  |      |      |      | 5%   |      |
| 8.2   |       |       |       |      |      | 100% |      |      |      |
| 8.4   |       |       |       | 2%   |      |      |      | 96%  |      |
| 8.5   |       |       |       | 5%   |      |      |      | 94%  |      |
| 14.7  |       |       |       |      |      | 37%  |      |      |      |
| 14.8  |       |       |       |      | 4%   | 44%  |      | 4%   |      |
| 15.5  |       |       |       |      |      | 23%  |      |      |      |
| 17.3  |       |       |       |      | 3%   | 64%  |      | 1%   |      |
| 17.4  |       |       |       |      | 2%   | 68%  |      | 1%   |      |
| 17.5  |       |       |       |      | 3%   | 67%  |      |      |      |
| 17.6  |       |       |       |      |      | 69%  |      |      |      |
| 17.7  |       |       |       |      |      | 69%  |      |      |      |
| 17.7  |       |       |       |      |      | 70%  |      |      |      |
| 19.1  |       |       |       |      | 2%   |      |      | 85%  |      |
| 19.6  |       |       |       | 1%   | 4%   |      |      | 89%  |      |
| 19.8  |       |       |       |      | 6%   |      |      | 90%  |      |
| 19.9  |       |       |       |      | 2%   |      |      | 93%  |      |
| 19.9  |       |       |       |      |      |      |      | 94%  |      |
| 20.0  |       |       |       |      | 3%   | 1%   |      | 93%  |      |
| 20.0  |       |       |       |      |      |      |      | 100% |      |
| 20.1  |       |       |       |      | 1%   |      |      | 95%  |      |
| 20.4  |       |       |       |      |      |      |      | 100% |      |
| 23.5  |       |       |       |      | 100% |      |      |      |      |
| 23.6  |       |       |       |      | 100% |      |      |      |      |
| 23.6  |       |       |       |      |      | 100% |      |      |      |
| 23.6  |       |       |       |      |      |      |      | 100% |      |
| 23.7  |       |       |       |      | 89%  |      | 2%   |      |      |
| 23.7  |       |       |       |      | 94%  |      | 3%   |      |      |
| 23.7  |       |       |       |      | 94%  |      |      |      |      |
Table S5. Molecular orbital (MO) composition of \( \text{NdBr}_3(\text{OPMe}_3)_3 \) for the following orbital populations: Nd – 5\( p \), 4\( f \), 5\( d \); O – 2\( s \), 2\( p \); Br – 4\( s \), 4\( p \); P – 3\( s \), 3\( p \). Percentages in bold represent the main contribution to the MO. Energies given are relative to the first O 2\( s \) MO.

| E (eV) | Nd 5\( p \) | Nd 4\( f \) | Nd 5\( d \) | O 2\( s \) | O 2\( p \) | Br 4\( s \) | Br 4\( p \) | P 3\( s \) | P 3\( p \) |
|--------|-------------|-------------|-------------|-----------|-----------|-----------|-----------|----------|----------|
| 0.0    | 4%          |             |             | 71%       | 3%        |           |           | 10%      | 5%       |
| 0.0    | 6%          |             |             | 70%       | 1%        |           |           | 10%      | 4%       |
| 0.3    |             |             |             | 72%       | 4%        |           |           | 12%      | 8%       |
| 3.6    | 82%         | 6%          |             |           |           |           |           | 5%       |          |
| 3.6    | 89%         | 3%          | 1%          | 3%        |           |           |           |          |          |
| 3.7    | 95%         |             |             |           |           | 3%        |           |          |          |
| 8.2    |             | 1%          |             |           |           |           | 99%       |          |          |
| 8.4    |             |             |             |           |           | 97%       |           |          |          |
| 8.4    | 3%          |             |             |           |           |           | 97%       |          |          |
| 14.8   | 4%          |             |             | 36%       |           |           |           |          |          |
| 14.8   |             |             |             | 4%        | 42%       |           |           | 4%       |          |
| 15.5   | 3%          |             |             | 6%        | 46%       |           |           | 6%       |          |
| 17.3   | 3%          |             |             |           | 64%       |           |           | 1%       |          |
| 17.5   | 2%          |             |             |           | 69%       |           |           | 1%       |          |
| 17.6   | 3%          |             |             |           | 65%       |           |           |          |          |
| 17.7   |             |             |             |           |           |           | 69%       |          |          |
| 17.7   |             |             |             |           |           |           | 68%       |          |          |
| 17.8   |             |             |             |           |           |           | 70%       |          |          |
| 19.1   | 6%          |             |             |           |           |           |           | 85%      |          |
| 19.6   | 2%          | 4%          |             |           |           |           |           | 88%      |          |
| 19.8   |             |             |             |           |           |           |           | 92%      |          |
| 19.9   | 4%          | 2%          |             |           |           |           |           | 92%      |          |
| 19.9   | 2%          |             |             |           |           |           |           | 94%      |          |
| 20.0   | 4%          | 2%          |             |           |           |           |           | 93%      |          |
| 20.0   |             |             |             |           |           |           |           | 94%      |          |
| 20.0   |             |             |             |           |           |           |           | 95%      |          |
| 20.4   |             |             |             |           |           |           |           | 98%      |          |
| 22.3   | 100%        |             |             |           |           |           |           |          |          |
| 22.3   | 100%        |             |             |           |           |           |           |          |          |
| 22.4   | 100%        |             |             |           |           |           |           |          |          |
| 22.4   | 100%        |             |             |           |           |           |           |          |          |
| 22.5   |             |             |             |           |           |           |           | 93%      | 2%       |
| 22.5   |             |             |             |           |           |           |           | 93%      | 4%       |
| 22.5   |             |             |             |           |           |           |           | 93%      | 4%       |

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Table S6. Slater-Condon parameters of the 5/6p semi-core electrons derived from LF-DFT for the free-ions, $[\text{M(H}_2\text{O)}_9]^3+$, and $\text{MBr}_3(\text{OPcy})_3$ complexes ($\text{M} = \text{Ce, Nd, Am}$).

|            | $F^2(p,p)$ (eV) | $\zeta_{5/6p}$ (eV) |
|------------|-----------------|---------------------|
| Free-ion   |                 |                     |
| $[\text{M(H}_2\text{O)}_9]^3+$ | 7.715 | 5.557 | 2.320 |
| $\text{MBr}_3(\text{OPcy})_3$ | 1.774 | 1.454 | 0.938 |
| Nd$^{\text{III}}$ | 7.970 | 6.259 | 4.520 |
| $\text{MBr}_3(\text{OPcy})_3$ | 2.063 | 1.754 | 1.492 |
| Am$^{\text{III}}$ | 7.583 | 6.112 | 4.207 |
| $\text{MBr}_3(\text{OPcy})_3$ | 5.818 | 4.985 | 4.259 |

Table S7. Natural localized molecular orbitals (NLMOs) involving pseudo-core 5s (6s), 5p (6p), and 4f (5f) electrons in $\text{MBr}_3(\text{OPMe})_3$ ($\text{M} = \text{Ce, Nd, Am}$). Uranyl has been also included as a reference structure with strong ITI.

| [UO$_2$]$^{2+}$ | NLMO composition | Natural hybrid orbital composition |
|------------------|------------------|-----------------------------------|
| NLMO (1)         | 100% U           | 99% 6p + 1% 5f                    |
| NLMO (2)         | 100% U           | 99% 6p + 1% 5f                    |
| NLMO (3)         | 100% U           | 98% 6s + 2% 6d                    |
| NLMO (4)         | 99.8% U          | 76% 6p + 24% 5f                   |
| NLMO (5)         | 0.2% O           | 2% 2s + 98% 2p                    |

CeBr$_3$(OPMe)$_3$ | NLMO composition | Natural hybrid orbital composition |
|------------------|------------------|-----------------------------------|
| NLMO (1)         | 100% Ce          | 98% 5p + 2% 4f                    |
| NLMO (2)         | 100% Ce          | 2% 5p + 98% 4f                    |
| NLMO (3)         | 99.8% Ce         | 59% 5s + 41% 5p                   |
|                  | *0.2% O, P       |                                   |
| NLMO (4)         | 99.5% Ce         | 41% 5s + 59% 5p                   |
|                  | *0.5% O, P       |                                   |
| NLMO (5)         | 99.3% Ce         | 100% 5p                           |
|                  | *0.7% O, P       |                                   |
| NdBr₃(OPMe₃)₃ | NLMO composition | Natural hybrid orbital composition |
|---------------|------------------|----------------------------------|
| NLMO (1)      | 99.9% Nd         | 100% 5p                          |
| NLMO (2)      | 99.8% Nd         | 55% 5s + 43% 5p + 2% 4f          |
|               | *0.2% O, P       |                                  |
| NLMO (3)      | 99.8% Nd         | 100% 4f                          |
|               | *0.2% O, P       |                                  |
| NLMO (4)      | 99.7% Nd         | 4% 5s + 96% 4f                   |
|               | *0.3% O, P       |                                  |
| NLMO (5)      | 99.6% Nd         | 2% 5s + 2% 5p + 96% 4f          |
|               | *0.4% O, P       |                                  |
| NLMO (6)      | 99.6% Nd         | 40% 5s + 54% 5p + 6% 4f         |
|               | *0.4% O, P       |                                  |
| NLMO (7)      | 99.5% Nd         | 100% 5p                          |
|               | *0.5% O, P       |                                  |

| AmBr₃(OPMe₃)₃ | NLMO composition | Natural hybrid orbital composition |
|---------------|------------------|----------------------------------|
| NLMO (1)      | 100% Am          | 98% 6p + 2% 5f                   |
| NLMO (2)      | 100% Am          | 2% 6s + 5% 6p + 93% 5f          |
| NLMO (3)      | 99.9% Am         | 44% 6s + 42% 6p + 14% 5f        |
|               | *0.1% O, P       |                                  |
| NLMO (4)      | 99.9% Am         | 31% 6s + 21% 6p + 48% 5f        |
|               | *0.1% O, P       |                                  |
| NLMO (5)      | 99.8% Am         | 11% 6s + 26% 6p + 63% 5f        |
|               | 0.2% O, P        |                                  |
| NLMO (6)      | 99.8% Am         | 32% 6p + 68% 5f                 |
|               | *0.2% O, P       |                                  |
| NLMO (7)      | 99.7% Am         | 9% 6s + 29% 6p + 62% 5f         |
|               | *0.3% O, P       |                                  |
| NLMO (8)      | 99.7% Am         | 2% 6s + 10% 6p + 88% 5f         |
|               | *0.3% O, P       |                                  |
| NLMO (9)      | 99.6% Am         | 1% 6s + 10% 6p + 89% 5f         |
|               | *0.4% O, P       |                                  |
| NLMO (10)     | 99.3% Am         | 28% 6p + 72% 5f                 |
|               | *0.7% O, P       |                                  |
O, P contributions are \( sp \) hybrid orbitals in different ratios, so they were not explicitly written for the sake of simplicity.

**All structures differ in number of NLMOs due to occupancy of \( f \)-electrons, i.e. in addition to the 4 orbitals \((3p + 1s)\) \( \text{U}^{6+} \) corresponds to an \( f^0 \) configuration, \( \text{Ce}^{3+} \) to an \( f^1 \), \( \text{Nd}^{3+} \) to an \( f^3 \), and \( \text{Am}^{3+} \) to an \( f^6 \), giving rise to 4, 5, 7, and 10 NLMOs, respectively.

**Table S8. NLMOs involving main Am–Ligand interactions in \( \text{CeBr}_3(\text{OPMe}_3)_3 \).**

| \( \text{CeBr}_3(\text{OPMe}_3)_3 \) | NLMO composition | Natural hybrid orbital composition |
|-------------------------------------|------------------|-----------------------------------|
| NLMO (6)                            | 2% Ce            | 1% \( 6s \) + 72% \( 5d \) + 27% \( 4f \) |
|                                     | 92% O1           | 100% \( 2p \)                     |
|                                     | 4% P1            | 76% \( 3p \) + 24% \( 3d \)       |
| NLMO (7)                            | 2% Ce            | 72% \( 5d \) + 28% \( 4f \)       |
|                                     | 92% O2           | 100% \( 2p \)                     |
|                                     | 4% P2            | 76% \( 3p \) + 24% \( 3d \)       |
| NLMO (8)                            | 2% Ce            | 71% \( 5d \) + 29% \( 4f \)       |
|                                     | 92% O3           | 100% \( 2p \)                     |
|                                     | 4% P3            | 76% \( 3p \) + 24% \( 3d \)       |
| NLMO (9)                            | 8% Ce            | 26% \( 6s \) + 57% \( 5d \) + 17% \( 4f \) |
|                                     | 92% Br1          | 31% \( 4s \) + 69% \( 4p \)      |
| NLMO (10)                           | 8% Ce            | 26% \( 6s \) + 57% \( 5d \) + 17% \( 4f \) |
|                                     | 87% Br2          | 31% \( 4s \) + 69% \( 4p \)      |
| NLMO (11)                           | 8% Ce            | 26% \( 6s \) + 57% \( 5d \) + 17% \( 4f \) |
|                                     | 89% Br3          | 31% \( 4s \) + 69% \( 4p \)      |
Table S9. NLMOs involving main Am–Ligand interactions in NdBr$_3$(OPMe$_3$)$_3$.

| NdBr$_3$(OPMe$_3$)$_3$ | NLMO composition | Natural hybrid orbital composition |
|------------------------|------------------|-----------------------------------|
| NLMO (8)               | 1% Nd            | 1% 6s + 81% 5d + 18% 4f           |
|                       | 92% O1           | 100% 2p                           |
|                       | 4% P1            | 76% 3p + 24% 3d                   |
| NLMO (9)               | 2% Nd            | 4% 6s + 71% 5d + 25% 4f           |
|                       | 92% O2           | 100% 2p                           |
|                       | 4% P2            | 76% 3p + 24% 3d                   |
| NLMO (10)              | 1% Nd            | 81% 5d + 19% 4f                   |
|                       | 92% O3           | 100% 2p                           |
|                       | 4% P3            | 77% 3p + 23% 3d                   |
| NLMO (11)              | 10% Nd           | 24% 6s + 49% 5d + 27% 4f          |
|                       | 92% Br1          | 24% 4s + 76% 4p                   |
| NLMO (12)              | 10% Nd           | 24% 6s + 50% 5d + 26% 4f          |
|                       | 87% Br2          | 24% 4s + 76% 4p                   |
| NLMO (13)              | 9% Nd            | 24% 6s + 51% 5d + 25% 4f          |
|                       | 89% Br3          | 25% 4s + 75% 4p                   |
**Table S10.** NLMOs involving main Am–Ligand interactions in $^{\text{AmBr}}_3(\text{OPMe}_3)_3$.

| $^{\text{AmBr}_3(\text{OPMe}_3)_3}$ | NLMO composition | Natural hybrid orbital composition |
|-----------------------------------|-----------------|----------------------------------|
| NLMO (11)                         | 3% Am           | 10% 7s + 51% 6d + 39% 5f         |
|                                   |                 | 91% O1                           | 3% 2s + 97% 2p                      |
|                                   |                 | 4% P1                            | 79% 3p + 21% 3d                    |
| NLMO (12)                         | 3% Am           | 9% 7s + 56% 6d + 35% 5f          |
|                                   |                 | 91% O2                           | 3% 2s + 97% 2p                      |
|                                   |                 | 4% P2                            | 79% 3p + 21% 3d                    |
| NLMO (13)                         | 3% Am           | 10% 7s + 48% 6d + 42% 5f         |
|                                   |                 | 91% O3                           | 3% 2s + 97% 2p                      |
|                                   |                 | 4% P3                            | 79% 3p + 21% 3d                    |
| NLMO (14)                         | 13% Am          | 22% 7s + 39% 6d + 39% 5f         |
|                                   |                 | 87% Br1                         | 17% 4s + 83% 4p                    |
| NLMO (15)                         | 13% Am          | 22% 7s + 40% 6d + 38% 5f         |
|                                   |                 | 87% Br2                         | 18% 4s + 82% 4p                    |
| NLMO (16)                         | 11% Am          | 24% 7s + 47% 6d + 29% 5f         |
|                                   |                 | 89% Br3                         | 21% 4s + 79% 4p                    |
Further Electronic Structure Discussion.

The ground and low-lying excited states in $\text{AmBr}_3(\text{OPcy}_3)_3$ were calculated to gain a better understanding what role the ligands play in bonding to americium. For comparison, the same calculations were performed on the cerium and neodymium complexes to determine the ground state multiplet splitting. The ground multiplet splitting in $\text{CeBr}_3(\text{OPcy}_3)_3$ corresponds to the usual $J = \frac{5}{2}$ for a Ce(III) complex, and is reflected in the splitting of the low-lying Kramer's doublets (KDs) at 831.5 cm$^{-1}$. The closest reported value is 1036.6 cm$^{-1}$ for $\{(\text{C}_8\text{H}_6(\text{SiMe}_3)_2)_2\text{Ce}\}^-$. A simple calculation of the free-Ce(III) ion shows a splitting of 2 cm$^{-1}$, which highlights the role of the phosphine oxide ligand. When the same analysis is performed on $\text{NdBr}_3(\text{OPcy}_3)_3$, a ground state $J = \frac{9}{2}$ multiplet that spans an energy window of 413.8 cm$^{-1}$ is calculated and is comparable to the ~495 cm$^{-1}$ experimentally determined value for Nd$_2$O$_3$ crystals. Unfortunately, this analysis cannot be performed for $\text{AmBr}_3(\text{OPcy}_3)_3$ because there is no splitting due to the $J = 0$ ground state. However, it is clear that the quasi-octahedral environment provides a strong ligand field environment capable of modifying the electronic properties of these complexes.
ITI COMPARISONS AND CALCULATIONS OF LITERATURE COMPOUNDS

Table S11. ITI Calculations of Newly Reported and Previously Reported LnBr₃(OPcy₃)₃ Compounds,a,b

|        | La³  | La³  | Ce³  | Pr³  | Pr³  | Nd³  | Nd³  | Gd³  | Ho³  |
|--------|------|------|------|------|------|------|------|------|------|
| Radius (Å) | 1.032 | 1.032 | 1.01 | 0.99 | 0.99 | 0.983| 0.983| 0.938| 0.901|
| ITI M–Br | 99.1(1) | 99.7(1) | 99.0(2) | 98.9(2) | 98.7(5) | 98.9(2) | 98.7(3) | 98.7(3) | 98.7(3) |
| ITI M–O  | 99.0(3) | 99.0(3) | 98.56(8) | 98.4(2) | 98.3(2) | 98.6(3) | 98.7(2) | 99.0(1) | 98.5(3) |

aGiven with calculated standard error in parentheses b6-Coordinate Shannon Ionic Radius.4 cThis work

Table S12. ITI Calculations of LnI₃(Et₂O)₃ Compounds,a,b

|        | Ce  | Pr  | Nd  | Sm  | Gd  | Tb  |
|--------|-----|-----|-----|-----|-----|-----|
| Radius (Å) | 1.01 | 0.99 | 0.983 | 0.958 | 0.938 | 0.923 |
| ITI M–I | 101.21(2) | 101.22(2) | 99.87[7] | 101.16(2) | 100.96(2) | 101.00(2) |
| ITI M–O | 95.8(1) | 95.4(2) | 97.6[7] | 95.1(2) | 96.1(1) | 95.9(2) |

aGiven with calculated standard errors in parentheses and propagated error in square brackets. b6-Coordinate Shannon Ionic Radius.4

Table S13. ITI Calculations of LnCl₃(HMPA)₃ Compounds,a,b

|        | Pr⁶ | Dy⁷ | Yb⁸ |
|--------|-----|-----|-----|
| Radius (Å) | 0.99 | 0.912 | 0.868 |
| ITI M–Cl | 100.8(1) | 100.4(1) | 100.3(1) |
| ITI M–O | 100.1(1) | 98.92(2) | 100.3(1) |

aGiven with calculated standard errors in parentheses. b6-Coordinate Shannon Ionic Radius.4

Table S14. ITI Calculations of YbX₃(THF)₃ Compounds,a

|        | Cl⁹ | Br¹⁰ | I¹¹ |
|--------|-----|------|-----|
| ITI M–X | 100.7(1) | 101.6[1] | 101.34[2] |
| ITI M–O | 96.9(5) | 96.8[5] | 97.3[3] |

aGiven with calculated standard errors in parentheses and propagated error in square brackets.
**CRYSTALLOGRAPHY**

**Table S15. Summary of Crystallographic Collections for MB₃(OPcy₃)₃.**

| Compound | Am | La | Ce | Pr | Nd |
|----------|----|----|----|----|----|
| **Empirical Formula** | C₅₄H₉₉O₃P₃Br₃Am | C₅₄H₉₉O₃P₃Br₃La | C₅₄H₉₉O₃P₃Br₃Ce | C₅₄H₉₉O₃.₅P₃Br₃Pr | C₅₄H₉₉O₃P₃Br₃Nd |
| **Temperature (K)** | 120(2) | 130(2) | 120(2) | 120(2) | 120(2) |
| **Crystal System** | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic |
| **Space Group** | Pca₂₁ | Pca₂₁ | Pca₂₁ | Pca₂₁ | Pca₂₁ |
| **a (Å)** | 28.768(9) | 28.879(2) | 28.920(5) | 28.716(1) | 28.706(1) |
| **b (Å)** | 11.456(4) | 11.4223(7) | 11.434(2) | 11.4126(4) | 11.4228(4) |
| **c (Å)** | 18.185(6) | 18.208(1) | 18.209(3) | 18.1299(8) | 18.1359(7) |
| **α(°)** | 90 | 90 | 90 | 90 | 90 |
| **β(°)** | 90 | 90 | 90 | 90 | 90 |
| **γ(°)** | 90 | 90 | 90 | 90 | 90 |
| **Volume (Å³)** | 5993(3) | 6006.3(6) | 6021(2) | 5941.5(4) | 5946.8(4) |
| **Z** | 4 | 4 | 4 | 4 | 4 |
| **ρcalcd (Mg/m³)** | 1.521 | 1.402 | 1.400 | 1.420 | 1.422 |
| **μ (mm⁻¹)** | 3.398 | 2.824 | 2.864 | 2.956 | 3.007 |
| **R1**<sup>a</sup> (I > 2.0σ(I)) | 0.0399 | 0.0348 | 0.0353 | 0.0317 | 0.0405 |
| **wR2** (all data) | 0.0858 | 0.0620 | 0.0726 | 0.0617 | 0.0777 |

| **BASF** | 0.02978 | 0.01767 | 0.03608 | 0.00891 | -0.00554 |

<sup>a</sup>Definitions:  
\[wR2 = \frac{\sum[w(F_o^2 - F_c^2)]}{\sum[w(F_o^2)]}^{1/2}\]
\[R1 = \frac{\sum||F_o| - |F_c||}{\sum|F_o|}\]

\[\text{Goof} = S = \frac{\sum[w(F_o^2 - F_c^2)]}{(n-p)}^{1/2}\] where \(n\) is the number of reflections and \(p\) is the total number of parameters refined.
Table S16. Relevant bond lengths [Å] and angles [°] for $\text{AmBr}_3(\text{OPcy}_3)_3$.  

| Bond/Angle | Value 1 | Value 2 | Value 3 | Value 4 |
|------------|---------|---------|---------|---------|
| Am(1)-Br(1) | 2.882(1) | O(1)-Am(1)-Br(2) | 89.73(19) |
| Am(1)-Br(2) | 2.870(1) | O(1)-Am(1)-Br(3) | 89.44(18) |
| Am(1)-Br(3) | 2.912(1) | O(1)-Am(1)-O(3) | 90.2(3) |
| Am(1)-O(1) | 2.312(7) | O(2)-Am(1)-Br(1) | 90.44(18) |
| Am(1)-O(2) | 2.302(7) | O(2)-Am(1)-Br(2) | 91.00(18) |
| Am(1)-O(3) | 2.349(6) | O(2)-Am(1)-Br(3) | 88.81(18) |
| P(1)-O(1) | 1.520(8) | O(2)-Am(1)-O(1) | 178.1(2) |
| P(2)-O(2) | 1.523(7) | O(2)-Am(1)-O(3) | 91.6(3) |
| P(3)-O(3) | 1.518(6) | O(3)-Am(1)-Br(1) | 87.6(2) |
| Br(1)-Am(1)-Br(3) | 95.60(5) | O(3)-Am(1)-Br(3) | 176.7(2) |
| Br(2)-Am(1)-Br(1) | 172.74(3) | P(1)-O(1)-Am(1) | 159.4(5) |
| Br(2)-Am(1)-Br(3) | 91.54(5) | P(2)-O(2)-Am(1) | 164.8(5) |
| O(1)-Am(1)-Br(1) | 89.05(18) | P(3)-O(3)-Am(1) | 170.8(5) |

Table S17. Relevant bond lengths [Å] and angles [°] for $\text{LaBr}_3(\text{OPcy}_3)_3$.  

| Bond/Angle | Value 1 | Value 2 | Value 3 | Value 4 |
|------------|---------|---------|---------|---------|
| La(1)-Br(1) | 2.9365(7) | O(1)-La(1)-Br(2) | 90.73(10) |
| La(1)-Br(2) | 2.9425(7) | O(1)-La(1)-Br(3) | 88.27(9) |
| La(1)-Br(3) | 2.9649(5) | O(1)-La(1)-O(2) | 178.16(13) |
| La(1)-O(1) | 2.351(4) | O(1)-La(1)-O(3) | 91.97(14) |
| La(1)-O(2) | 2.363(4) | O(2)-La(1)-Br(1) | 89.62(10) |
| La(1)-O(3) | 2.382(3) | O(2)-La(1)-Br(2) | 88.79(10) |
| P(1)-O(1) | 1.511(4) | O(2)-La(1)-Br(3) | 90.01(10) |
| P(2)-O(2) | 1.513(4) | O(2)-La(1)-O(3) | 89.78(15) |
| P(3)-O(3) | 1.513(3) | O(3)-La(1)-Br(1) | 85.23(12) |
| Br(1)-La(1)-Br(2) | 172.59(2) | O(3)-La(1)-Br(3) | 176.61(12) |
| Br(1)-La(1)-Br(3) | 91.39(3) | O(1)-O(1)-La(1) | 166.3(2) |
| Br(2)-La(1)-Br(3) | 95.84(3) | P(2)-O(2)-La(1) | 160.7(2) |
| O(1)-La(1)-Br(1) | 91.08(10) | P(3)-O(3)-La(1) | 170.9(3) |
### Table S18. Relevant bond lengths [Å] and angles [°] for CeBr₃(OPcy₃)₃.

| Bond                  | Length  | Angle     | Value   |
|-----------------------|---------|-----------|---------|
| Ce(1)-Br(1)           | 2.9268(8)| O(1)-Ce(1)-Br(2) | 91.16(10) |
| Ce(1)-Br(2)           | 2.9166(8)| O(1)-Ce(1)-Br(3) | 88.33(11) |
| Ce(1)-Br(3)           | 2.9504(8)| O(1)-Ce(1)-O(2) | 177.66(14) |
| Ce(1)-O(1)            | 2.332(4) | O(1)-Ce(1)-O(3) | 92.37(16)  |
| Ce(1)-O(2)            | 2.336(4) | O(2)-Ce(1)-Br(1) | 89.08(11) |
| Ce(1)-O(3)            | 2.368(4) | O(2)-Ce(1)-Br(2) | 89.55(11) |
| P(1)-O(1)             | 1.516(4) | O(2)-Ce(1)-Br(3) | 89.42(11) |
| P(2)-O(2)             | 1.515(4) | O(2)-Ce(1)-O(3) | 89.91(16) |
| P(3)-O(3)             | 1.523(4) | O(3)-Ce(1)-Br(1) | 87.42(13) |
| Br(1)-Ce(1)-Br(3)     | 95.47(3) | O(3)-Ce(1)-Br(2) | 85.48(13) |
| Br(2)-Ce(1)-Br(1)     | 172.78(2)| P(1)-O(1)-Ce(1) | 166.2(3)  |
| Br(2)-Ce(1)-Br(3)     | 91.61(3) | P(2)-O(2)-Ce(1) | 171.2(3)  |
| O(1)-Ce(1)-Br(1)      | 90.50(10)| P(3)-O(3)-Ce(1) | 160.7(3)  |

### Table S19. Relevant bond lengths [Å] and angles [°] for PrBr₃(OPcy₃)₃.

| Bond                  | Length  | Angle     | Value   |
|-----------------------|---------|-----------|---------|
| Pr(1)-Br(1)           | 2.8781(7)| O(1)-Pr(1)-Br(2) | 90.53(10) |
| Pr(1)-Br(2)           | 2.8894(7)| O(1)-Pr(1)-Br(3) | 88.55(10) |
| Pr(1)-Br(3)           | 2.9145(5)| O(1)-Pr(1)-O(2) | 177.63(13)|
| Pr(1)-O(1)            | 2.294(4) | O(1)-Pr(1)-O(3) | 92.17(15) |
| Pr(1)-O(2)            | 2.302(4) | O(2)-Pr(1)-Br(1) | 89.61(10) |
| Pr(1)-O(3)            | 2.336(3) | O(2)-Pr(1)-Br(2) | 89.18(10) |
| P(1)-O(1)             | 1.514(4) | O(2)-Pr(1)-Br(3) | 89.13(10) |
| P(2)-O(2)             | 1.515(4) | O(2)-Pr(1)-O(3) | 90.17(15) |
| P(3)-O(3)             | 1.510(3) | O(3)-Pr(1)-Br(1) | 85.72(12) |
| Br(1)-Pr(1)-Br(2)     | 173.18(2)| O(3)-Pr(1)-Br(3) | 87.57(12) |
| Br(1)-Pr(1)-Br(3)     | 91.37(3) | P(1)-O(1)-Pr(1) | 165.4(3)  |
| Br(2)-Pr(1)-Br(3)     | 95.32(2) | P(2)-O(2)-Pr(1) | 159.6(3)  |
| O(1)-Pr(1)-Br(1)      | 90.95(10)| P(3)-O(3)-Pr(1) | 171.0(3)  |
Table S20. Relevant bond lengths [Å] and angles [°] for NdBr$_3$(OPcy$_3$)$_3$.

| Bond                  | Distance | Angle       |
|-----------------------|----------|-------------|
| Nd(1)-Br(1)           | 2.8796(8) | O(1)-Nd(1)-Br(2) | 90.45(13) |
| Nd(1)-Br(2)           | 2.8908(9) | O(1)-Nd(1)-Br(3) | 88.59(12) |
| Nd(1)-Br(3)           | 2.9168(6) | O(1)-Nd(1)-O(2) | 177.70(16) |
| Nd(1)-O(1)            | 2.297(5)  | O(1)-Nd(1)-O(3) | 92.20(19)  |
| Nd(1)-O(2)            | 2.309(5)  | O(2)-Nd(1)-Br(1) | 89.81(14) |
| Nd(1)-O(3)            | 2.336(4)  | O(2)-Nd(1)-Br(2) | 88.95(13) |
| P(1)-O(1)             | 1.513(5)  | O(2)-Nd(1)-Br(3) | 89.26(13) |
| P(2)-O(2)             | 1.511(5)  | O(2)-Nd(1)-O(3) | 89.99(19) |
| P(3)-O(3)             | 1.513(4)  | O(3)-Nd(1)-Br(1) | 85.78(15) |
|                      |          | O(3)-Nd(1)-Br(2) | 87.49(15) |
| Br(1)-Nd(1)-Br(2)     | 173.15(3) | O(3)-Nd(1)-Br(3) | 177.06(14) |
| Br(1)-Nd(1)-Br(3)     | 91.38(3)  | P(1)-O(1)-Nd(1)  | 165.2(3)  |
| Br(2)-Nd(1)-Br(3)     | 95.34(3)  | P(2)-O(2)-Nd(1)  | 159.2(3)  |
| O(1)-Nd(1)-Br(1)      | 91.04(13) | P(3)-O(3)-Nd(1)  | 171.2(3)  |
X-ray Data Collection, Structure Solution and Refinement for AmBr$_3$(OPcy$_3$)$_3$.

An amber crystal of approximate dimensions 0.06 x 0.12 x 0.196 mm was mounted on a nylon loop and transferred to a Bruker D8 Quest diffractometer. The APEX3\textsuperscript{12} program package was used to determine the unit-cell parameters and for data collection (17 sec/frame scan time for a calculated scan of diffraction data and a detector distance of 41 mm). The raw frame data was processed using SAINT\textsuperscript{13} and SADABS\textsuperscript{14} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL\textsuperscript{15} or OLEX2\textsuperscript{16} program. The diffraction symmetry was $mmm$ and the systematic absences were consistent with the orthorhombic space groups $Pbcm$ and $Pca_2_1$. It was later determined that space group $Pca_2_1$ was correct.

The initial structure was solved by direct methods using Pu in place of Am, since Am is not recognized by APEX3. The structure was refined on $F^2$ by full-matrix least-squares techniques using Am, the scattering factors for which were taken from the International Tables for Crystallography Volume C.\textsuperscript{17} The analytical scattering factors for neutral atoms were used throughout the analysis.\textsuperscript{17} Hydrogen atoms were included using a riding model.

The absolute structure was assigned by refinement of the Flack parameter.\textsuperscript{18} Based on the Flack parameter, the data was refined as a 2-component twin with BASF = 0.02978. The compound was found to isomorphous with its lanthanide analogs: Pr (BUGRIG),\textsuperscript{3} Nd (BUGROM),\textsuperscript{3} Gd (BUGRUS),\textsuperscript{3} Ho (ROVNUN),\textsuperscript{3} which are all reported as a hemi-hydrate, which was not located in the Fourier map for Am.

**Figure S44.** Thermal ellipsoid plot of AmBr$_3$(OPcy$_3$)$_3$ drawn at the 50% probability level with hydrogen atoms omitted for clarity.
**Table S21.** Crystal data and structure refinement for $\text{AmBr}_3(\text{OPcy}_3)_3$.

| Property                                      | Value/Details                                      |
|-----------------------------------------------|----------------------------------------------------|
| Identification code                           | cjw84 (Cory Windorff)                              |
| Empirical formula                             | $\text{C}_{54}\text{H}_{99}\text{O}_3\text{P}_3\text{Br}_3\text{Am}$ |
| Formula weight                                 | 1371.97                                            |
| Temperature                                    | 120(2) K                                          |
| Wavelength                                     | 0.71073 Å                                         |
| Crystal system                                 | Orthorhombic                                      |
| Space group                                    | $Pca2_1$                                          |
| Unit cell dimensions                           |                                                   |
| a                                             | 28.768(9) Å                                      |
| α                                             | 90°                                                |
| b                                             | 11.456(4) Å                                      |
| β                                             | 90°                                                |
| c                                             | 18.185(6) Å                                      |
| γ                                             | 90°                                                |
| Volume                                         | 5993(3) Å $^3$                                    |
| Z                                             | 4                                                  |
| Density (calculated)                           | 1.521 Mg/m$^3$                                    |
| Absorption coefficient                         | 3.398 mm$^{-1}$                                   |
| F(000)                                        | 2768                                              |
| Crystal color                                  | clear yellow                                      |
| Crystal size                                   | 0.196 x 0.12 x 0.06 mm$^3$                        |
| Theta range for data collection                | 2.217 to 27.521°                                  |
| Index ranges                                   | $-35 \leq h \leq 37, -14 \leq k \leq 14, -23 \leq l \leq 20$ |
| Reflections collected                          | 70455                                             |
| Independent reflections                        | 12088 [R(int) = 0.0751]                            |
| Completeness to theta = 25.242°                | 99.9 %                                             |
| Absorption correction                          | Semi–empirical from equivalents                   |
| Max. and min. transmission                     | 0.0949 and 0.0640                                 |
| Refinement method                              | Full–matrix least–squares on F$^2$                |
| Data / restraints / parameters                 | 12088 / 1 / 578                                   |
| Goodness-of-fit on F$^2$                       | 1.081                                             |
| Final R indices [I>2sigma(I) = 9606 data]      | R1 = 0.0399, wR2 = 0.0787                          |
| R indices (all data, 0.77 Å)                   | R1 = 0.0606, wR2 = 0.0858                          |
| Absolute structure parameter                   | 0.004(7)                                          |
| Largest diff. peak and hole                    | 2.033 and −2.008 e.$\text{Å}^{-3}$                |
| BASF                                           | 0.02978                                           |

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X-ray Data Collection, Structure Solution and Refinement for LaBr$_3$(OPcy$_3$)$_3$.

A colorless crystal of approximate dimensions 0.153 x 0.157 x 0.267mm was mounted on a nylon loop and transferred to a Bruker D8 Quest diffractometer. The APEX3$^{12}$ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a calculated scan of diffraction data and a detector distance of 33 mm). The raw frame data was processed using SAINT$^{13}$ and SADABS$^{14}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL$^{15}$ or OLEX2$^{16}$ program. The diffraction symmetry was $mmm$ and the systematic absences were consistent with the orthorhombic space groups $Pbcm$ and $Pca_2_1$. It was later determined that space group $Pca_2_1$ was correct.

The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis.$^{17}$ Hydrogen atoms were included using a riding model.

The absolute structure was assigned by refinement of the Flack parameter.$^{18}$ Based on the Flack parameter, the data was refined as a 2-component twin with BASF = 0.01767. The compound was not isomorphous with its previous report (BUGREC),$^3$ and was found to isomorphous with its other lanthanide analogs: Pr (BUGRIG),$^3$ Nd (BUGROM),$^3$ Gd (BUGRUS),$^3$ and Ho (ROVNUN),$^3$ which are all reported as a hemi-hydrate, which was not located in the Fourier map for La.

**Figure S45.** Thermal ellipsoid plot of LaBr$_3$(OPcy$_3$)$_3$ drawn at the 50% probability level with hydrogen atoms omitted for clarity.
| **Crystal data and structure refinement for LaBr$_3$(OPcy)$_3$$_3$.** |
|---------------------------------------------------------------|
| **Identification code** | cjw86 (Cory Windorff) |
| **Empirical formula** | C$_{54}$H$_{99}$O$_3$P$_3$Br$_3$La |
| **Formula weight** | 1267.88 |
| **Temperature** | 130(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal system** | Orthorhombic |
| **Space group** | $Pca2_1$ |
| **Unit cell dimensions** | a = 28.8790(16) Å, $\alpha = 90^\circ$.  
b = 11.4223(7) Å, $\beta = 90^\circ$.  
c = 18.2083(10) Å, $\gamma = 90^\circ$. |
| **Volume** | 6006.3(6) Å$^3$ |
| **Z** | 4 |
| **Density (calculated)** | 1.402 Mg/m$^3$ |
| **Absorption coefficient** | 2.824 mm$^{-1}$ |
| **F(000)** | 2616 |
| **Crystal color** | clear colorless |
| **Crystal size** | 0.267 x 0.157 x 0.153 mm$^3$ |
| **Theta range for data collection** | 2.220 to 27.545$^\circ$ |
| **Index ranges** | $-37 \leq h \leq 37$, $-14 \leq k \leq 14$, $-22 \leq l \leq 23$ |
| **Reflections collected** | 109745 |
| **Independent reflections** | 13561 [R(int) = 0.0669] |
| **Completeness to theta = 25.50$^\circ$** | 99.9 % |
| **Absorption correction** | Semi–empirical from equivalents |
| **Max. and min. transmission** | 0.7456 and 0.6638 |
| **Refinement method** | Full–matrix least–squares on F$^2$ |
| **Data / restraints / parameters** | 13561 / 1 / 578 |
| **Goodness-of-fit on F$^2$** | 1.092 |
| **Final R indices [I>2sigma(I) = 11489 data]** | R1 = 0.0348, wR2 = 0.0566 |
| **R indices (all data, 0.77 Å)** | R1 = 0.0510, wR2 = 0.0620 |
| **Absolute structure parameter** | 0.018(9) |
| **Largest diff. peak and hole** | 0.757 and $-0.569$ e.Å$^{-3}$ |
| **BASF** | 0.01767 |
X-ray Data Collection, Structure Solution and Refinement for CeBr₃(OPcy₃)₃.

An orange crystal of approximate dimensions 0.123 x 0.156 x 0.268 mm was mounted on a nylon loop and transferred to a Bruker D8 Quest diffractometer. The APEX³ program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time for a calculated scan of diffraction data and a detector distance of 42 mm). The raw frame data was processed using SAINT¹³ and SADABS¹⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL¹⁵ or OLEX2¹⁶ program. The diffraction symmetry was mmm and the systematic absences were consistent with the orthorhombic space groups Pbcm and Pca₂₁. It was later determined that space group Pca₂₁ was correct.

The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis.¹⁷ Hydrogen atoms were included using a riding model.

The absolute structure was assigned by refinement of the Flack parameter.¹⁸ Based on the Flack parameter, the data was refined as a 2-component twin with BASF = 0.03608. The compound is isomorphous with its other lanthanide analogs: Pr (BUGRIG),³ Nd (BUGROM),³ Gd (BUGRUS),³ and Ho (ROVNUN),³ which are all reported as a hemihydrate, which was not located in the Fourier map for Ce.

Figure S46. Thermal ellipsoid plot of CeBr₃(OPcy₃)₃ drawn at the 50% probability level with hydrogen atoms omitted for clarity.
Table S23. Crystal data and structure refinement for CeBr₃(OPcy)₃.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                           | cjw61 (Cory Windorff)                      |
| Empirical formula                             | C₅₄H₉₉O₃P₃Br₃Ce                           |
| Formula weight                                 | 1269.09                                   |
| Temperature                                    | 120(2) K                                  |
| Wavelength                                    | 0.71073 Å                                 |
| Crystal system                                 | Orthorhombic                              |
| Space group                                    | Pca2₁                                     |
| Unit cell dimensions                          | a = 28.920(5) Å, b = 11.434(2) Å, c = 18.209(3) Å |
| Volume                                        | 6021.2(18) Å³                             |
| Z                                             | 4                                         |
| Density (calculated)                          | 1.400 Mg/m³                               |
| Absorption coefficient                        | 2.864 mm⁻¹                                |
| F(000)                                        | 2620                                      |
| Crystal color                                 | clear orange                              |
| Crystal size                                  | 0.268 x 0.156 x 0.123 mm³                 |
| Theta range for data collection               | 2.218 to 27.511°                          |
| Index ranges                                  | −37 ≤ h ≤ 37, −14 ≤ k ≤ 14, −23 ≤ l ≤ 23  |
| Reflections collected                         | 122286                                    |
| Independent reflections                       | 13805 [R(int) = 0.0685]                   |
| Completeness to theta = 25.242°               | 99.9 %                                    |
| Absorption correction                         | Semi–empirical from equivalents           |
| Max. and min. transmission                    | 0.7456 and 0.6448                         |
| Refinement method                             | Full–matrix least–squares on F²           |
| Data / restraints / parameters                 | 13805 / 1 / 578                           |
| Goodness-of-fit on F²                          | 1.057                                     |
| Final R indices [I>2sigma(I) = 11775 data]    | R1 = 0.0353, wR2 = 0.0664                 |
| R indices (all data, 0.77 Å)                  | R1 = 0.0499, wR2 = 0.0726                 |
| Absolute structure parameter                  | −0.001(4)                                 |
| Largest diff. peak and hole                   | 0.956 and −0.784 e.Å⁻³                    |
| BASF                                          | 0.03608                                   |
X-ray Data Collection, Structure Solution and Refinement for PrBr$_3$(OPcy$_3$)$_3$.

A colorless crystal of approximate dimensions 0.315 x 0.205 x 0.188 mm was mounted on a nylon loop and transferred to a Bruker D8 Quest diffractometer. The APEX3$^{12}$ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a calculated scan of diffraction data at a detector distance of 35 mm). The raw frame data was processed using SAINT$^{13}$ and SADABS$^{14}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL$^{15}$ or OLEX2$^{16}$ program. The diffraction symmetry was $mmm$ and the systematic absences were consistent with the orthorhombic space groups $Pbcm$ and $Pca2_1$. It was later determined that space group $Pca2_1$ was correct.

The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis.$^{17}$ Hydrogen atoms were included using a riding model.

The absolute structure was assigned by refinement of the Flack parameter.$^{18}$ Based on the Flack parameter, the data was refined as a 2-component twin with BASF = 0.00891. The compound is a redetermination of the previously data (BUGRIG),$^3$ and is isomorphous with its other lanthanide analogs: Nd (BUGROM),$^3$ Gd (BUGRUS),$^3$ and Ho (ROVNUN).$^3$

![Figure S47. Thermal ellipsoid plot of PrBr$_3$(OPcy$_3$)$_3$ drawn at the 50% probability level with hydrogen atoms (and lattice solvent) omitted for clarity.](image-url)
Table S24. Crystal data and structure refinement for $\text{PrBr}_3(\text{OPcy}_3)_3$.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                           | cjw94 (Cory Windorff)                      |
| Empirical formula                             | $\text{C}_{54}\text{H}_{99}\text{O}_3\text{P}_3\text{Br}_3\text{Pr}$ |
| Formula weight                                | 1269.88                                    |
| Temperature                                   | 120(2) K                                   |
| Wavelength                                    | 0.71073 Å                                  |
| Crystal system                                | Orthorhombic                               |
| Space group                                   | $Pca2_1$                                   |
| Unit cell dimensions                          | $a = 28.716(1)$ Å, $\alpha = 90^\circ$.    |
|                                             | $b = 11.4126(4)$ Å, $\beta = 90^\circ$.    |
|                                             | $c = 18.1299(8)$ Å, $\gamma = 90^\circ$.   |
| Volume                                        | 5941.5(4) Å                                |
| $Z$                                           | 4                                          |
| Density (calculated)                          | 1.420 Mg/m³                                 |
| Absorption coefficient                        | 2.956 mm⁻¹                                 |
| $F(000)$                                      | 2624                                       |
| Crystal color                                 | clear colorless                            |
| Crystal size                                  | 0.315 x 0.205 x 0.188 mm³                  |
| Theta range for data collection               | 2.225 to 27.551°                           |
| Index ranges                                  | $-37 \leq h \leq 37$, $-14 \leq k \leq 14$, $-23 \leq l \leq 23$ |
| Reflections collected                         | 106432                                     |
| Independent reflections                       | 13677 [R(int) = 0.0613]                    |
| Completeness to theta                         | 25.500°                                    |
| Absorption correction                         | Semi-empirical from equivalents            |
| Max. and min. transmission                    | 0.7456 and 0.6775                          |
| Refinement method                             | Full-matrix least-squares on $F^2$         |
| Data / restraints / parameters                 | 13677 / 1 / 578                           |
| Goodness-of-fit on $F^2$                      | 1.055                                      |
| Final R indices [I>2sigma(I) = 11537 data]    | $R_1 = 0.0317$, $wR_2 = 0.0556$             |
| R indices (all data, 0.77 Å)                  | $R_1 = 0.0481$, $wR_2 = 0.0617$             |
| Absolute structure parameter                  | 0.009(9)                                   |
| Largest diff. peak and hole                    | 0.990 and $-0.720$ e.Å⁻³                   |
| BASF                                          | 0.00891                                    |
X-ray Data Collection, Structure Solution and Refinement for NdBr$_3$(OPcy$_3$)$_3$.

A colorless crystal of approximate dimensions 0.224 x 0.202 x 0.170 mm was mounted on a nylon loop and transferred to a Bruker D8 Quest diffractometer. The APEX3$^{12}$ program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time for a hemisphere of diffraction data with a scan width of 0.5° and a detector distance of 35 mm). The raw frame data was processed using SAINT$^{13}$ and SADABS$^{14}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL$^{15}$ or OLEX2$^{16}$ program. The diffraction symmetry was $mmm$ and the systematic absences were consistent with the orthorhombic space groups $Pbcm$ and $Pca_2_1$. It was later determined that space group $Pca_2_1$ was correct.

The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis.$^{17}$ Hydrogen atoms were included using a riding model.

The absolute structure was assigned by refinement of the Flack parameter.$^{18}$ Based on the Flack parameter, the data was refined as a 2-component twin with BASF = -0.00554. The structure is known (BUGROM)$^3$ and was re-determined. The compound is isomorphous with its other lanthanide analogs: Pr (BUGRIG),$^3$ Gd (BUGRS),$^3$ and Ho (ROVNUN),$^3$ which are all reported as a hemihydrate, which was not located in the Fourier map for Nd.

*Figure S48.* Thermal ellipsoid plot of NdBr$_3$(OPcy$_3$)$_3$ drawn at the 50% probability level with hydrogen atoms omitted for clarity.
Table S25. Crystal data and structure refinement for \(\text{NdBr}_3(\text{OPcy}_3)_3\).

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                           | cjw93 (Cory Windorff)                      |
| Empirical formula                             | \(C_{54}H_{99}O_3P_3Br_3Nd\)               |
| Formula weight                                | 1273.21                                    |
| Temperature                                   | 120(2) K                                   |
| Wavelength                                    | 0.71073 Å                                  |
| Crystal system                                | Orthorhombic                               |
| Space group                                   | \(Pca2_1\)                                 |
| Unit cell dimensions                          | \(a = 28.7074(14) \text{ Å}, \alpha = 90^\circ\) |
|                                              | \(b = 11.4137(6) \text{ Å}, \beta = 90^\circ\) |
|                                              | \(c = 18.1291(10) \text{ Å}, \gamma = 90^\circ\) |
| Volume                                        | 5946.8(4) Å                                 |
| \(Z\)                                         | 4                                          |
| Density (calculated)                          | 1.422 Mg/m³                                 |
| Absorption coefficient                        | 3.007 mm\(^{-1}\)                          |
| \(F(000)\)                                    | 2628                                       |
| Crystal color                                 | clear colorless                            |
| Crystal size                                  | 0.224 x 0.202 x 0.170 mm³                  |
| Theta range for data collection               | 2.223 to 27.557°                           |
| Index ranges                                  | \(-37 \leq h \leq 37, -14 \leq k \leq 14, -22 \leq l \leq 23\) |
| Reflections collected                         | 106339                                     |
| Independent reflections                       | 13649 [R(int) = 0.0874]                    |
| Completeness to theta                         | 99.9 %                                     |
| Absorption correction                         | Semi-empirical from equivalents            |
| Max. and min. transmission                    | 0.7456 and 0.6784                          |
| Refinement method                             | Full-matrix least-squares on \(F^2\)       |
| Data / restraints / parameters                 | 13649 / 1 / 578                            |
| Goodness-of-fit on \(F^2\)                    | 1.037                                      |
| Final R indices \([I>2\sigma(I) = 11307\text{ data}]\) | \(R_1 = 0.0405, wR_2 = 0.0680\)            |
| \(R\) indices (all data, 0.77 Å)             | \(R_1 = 0.0608, wR_2 = 0.0777\)            |
| Absolute structure parameter                  | -0.006(12)                                 |
| Largest diff. peak and hole                    | 1.021 and \(-1.569\) e.Å\(^{-3}\)         |
| BASF                                          | -0.00554                                   |

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