Electronic Supplementary Material (ESI) for Dalton Transactions

Structures, host-guest chemistry and mechanism of stepwise self-assembly of M_4L_6 tetrahedral cage complexes

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Supporting information

Part 1: Crystal structures of $[Ni_4(L^{bip})_6](BF_4)_8 \bullet 6MeNO_2$ and $[Zn_4(L^{bip})_6](BF_4)_8 \bullet 5MeNO_2$

Part 2: Details of the UV/Vis spectroscopic titrations and subsequent data analysis

Part 1: Crystal structures of $[Ni_4(L^{bip})_6](BF_4)_8 \bullet 6MeNO_2$ and $[Zn_4(L^{bip})_6](BF_4)_8 \bullet 5MeNO_2$

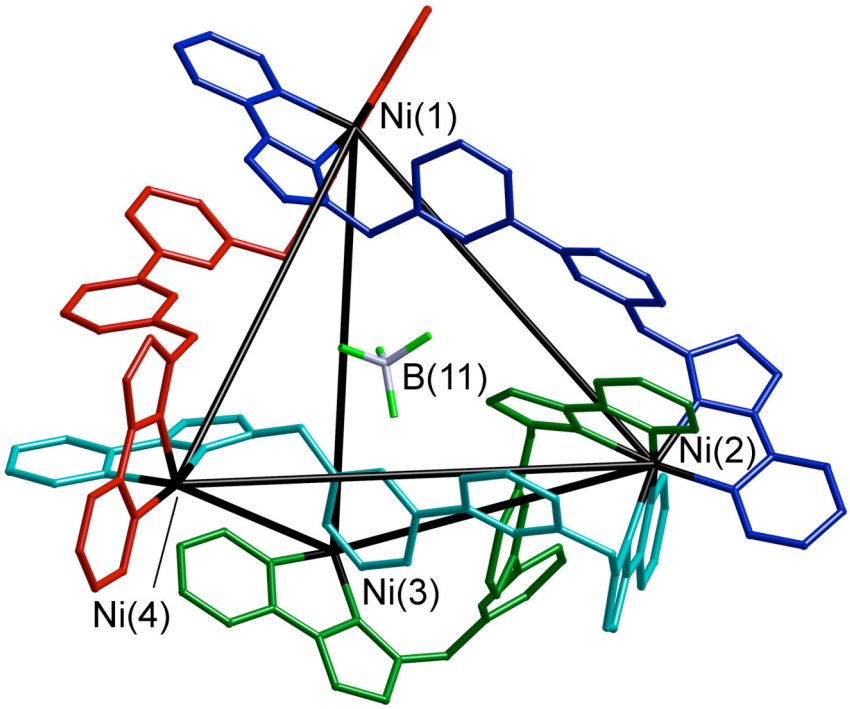


Fig. S1: Structure of one of the independent cage cations of $[Ni_4(L^{bip})_6](BF_4)_8 \bullet 6MeNO_2$ with two of the ligands removed for clarity, showing the encapsulated anion. Ni•••N distances lie in the range 2.04 – 2.14 Å; Ni•••Ni distances along the cage edges lie in the range 11.46 – 12.39 Å.

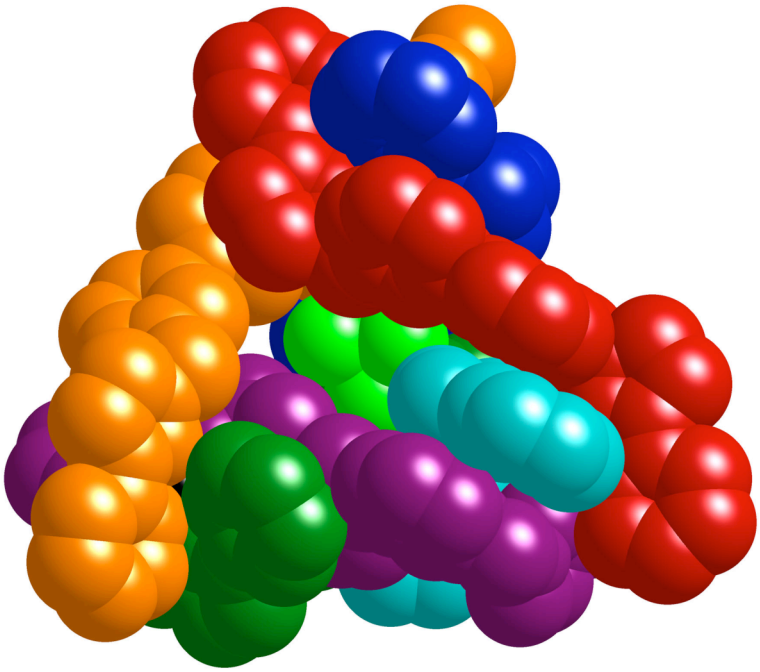


Fig. S2: Space-filling view of the above complex cation with its encapsulated anion (visible in pale green).

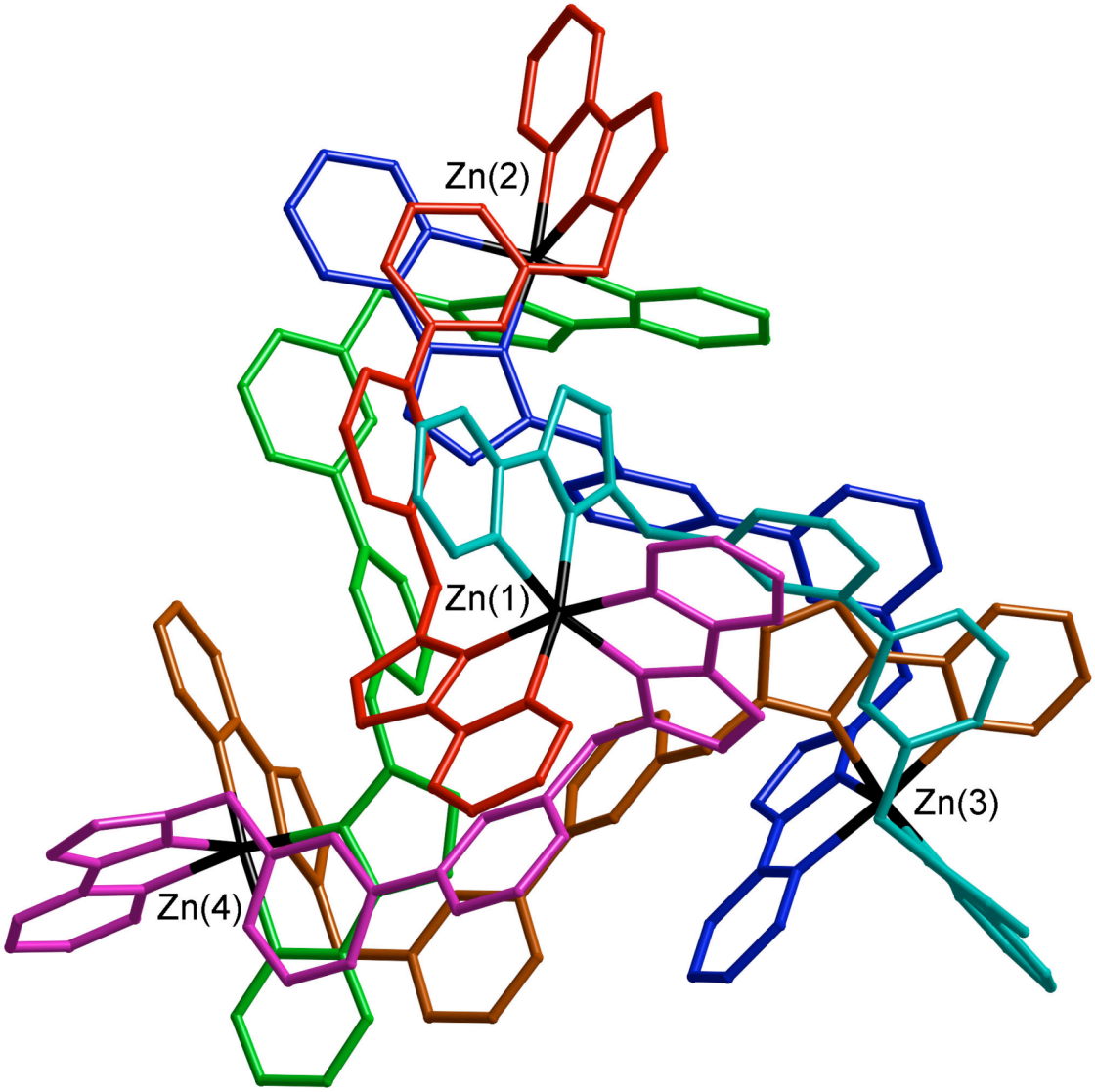
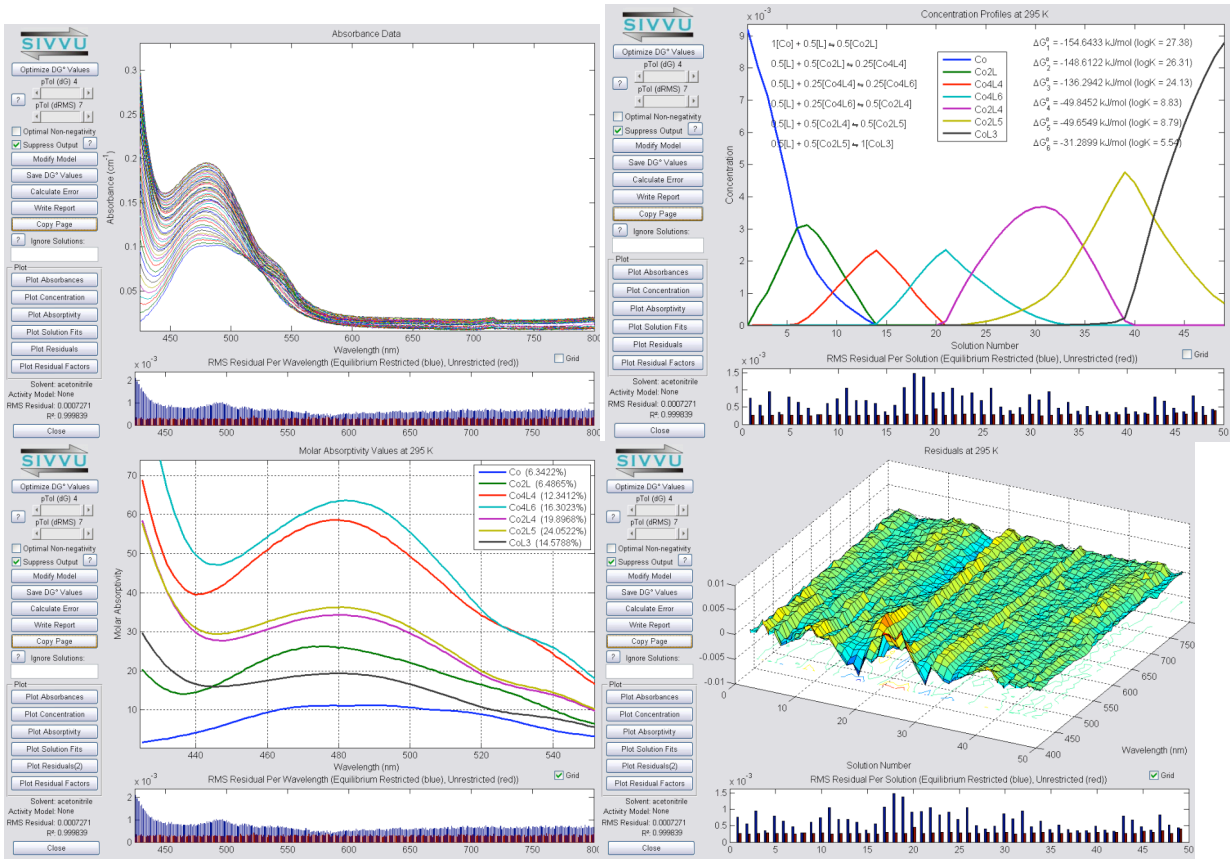


Fig. S3: Structure of cage cations of $[Zn_4(L^{bip})_6](BF_4)_8 \bullet 5MeNO_2$ looking on to the *fac* tris-chelate metal centre Zn(1), *i.e.* down the (non-crystallographic) C_3 axis. Zn•••N distances lie in the range 2.07 – 2.26 Å; Zn•••Zn distances along the cage edges lie in the range 11.56 – 12.18 Å.

Part 2: Details of the UV/Vis spectroscopic titrations and subsequent data analysis

(a) Titration of 0.010 0M $Co(BF_4)_2$ with 0 to 2.9 equivalents of L^{bip} at 295 K.



Optimization Summary:
Data at 295 K
Non-negativity was enforced with truncation (not optimization).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): $\Delta G°_1$ = -154.6(1); $\Delta G°_2$ = -148.6(1); $\Delta G°_3$ = -136.2(2);
$\Delta G°_4$ = -49.8(1); $\Delta G°_5$ = -49.6(1); $\Delta G°_6$ = -31.3(2);
Equilibrium Restricted RMS Residual (7 chemical factors): 0.0007271
Unrestricted RMS Residual (7 mathematical factors): 0.00028824
Restricted Data Reconstruction (7 chemical factors): 97.7182%
Unrestricted Data Reconstruction (7 mathematical factors): 97.9795%
Remaining Error Imbedded in Absorbance Values: 0.00029684
R^2: 99.9839%

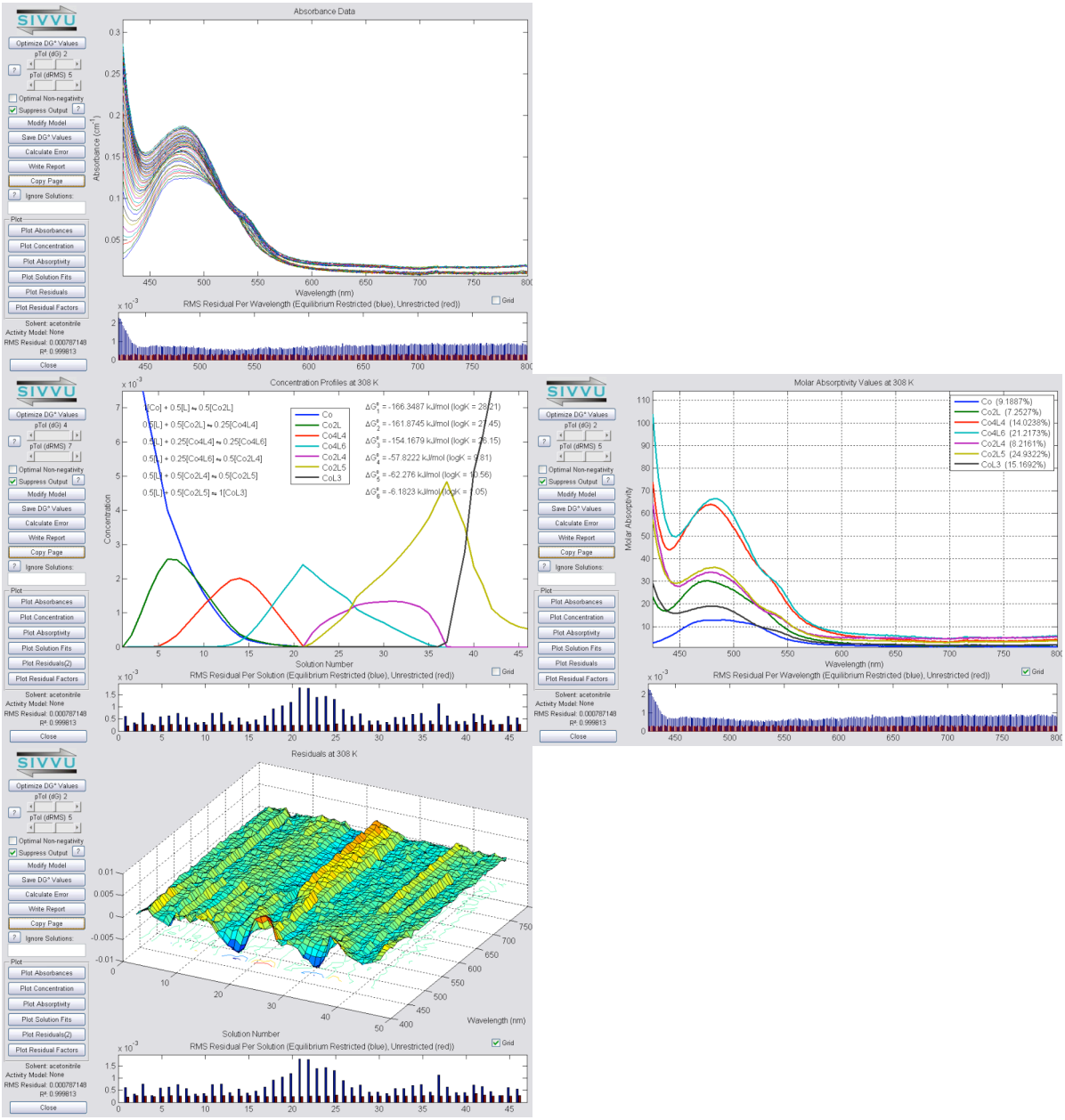
Estimating model sensitivity to DG values...
Each DG value is changed by 1 kJ/mol in both directions.
The resulting average change in RMS Residual corresponds to how sensitive the model is to that particular DG value.
When DG1 is shifted, the RMS residual increases by: 0.085101%
When DG2 is shifted, the RMS residual increases by: 0.086014%
When DG3 is shifted, the RMS residual increases by: 0.00090134%
When DG4 is shifted, the RMS residual increases by: 0.34169%
When DG5 is shifted, the RMS residual increases by: 0.34077%

When DG6 is shifted, the RMS residual increases by: 0.0016181%

Then, each DG value is changed again, but now the others are allowed to reoptimize. The resulting change in RMS Residual corresponds to how independent that particular DG value is. Vanishingly small or negative values indicate that only the difference between DG values is known accurately.

When DG1 is shifted, the RMS residual increases by: 3.9515e-012%
When DG2 is shifted, the RMS residual increases by: 7.1351e-011%
When DG3 is shifted, the RMS residual increases by: 2.4244e-010%
When DG4 is shifted, the RMS residual increases by: -1.3088e-010%
When DG5 is shifted, the RMS residual increases by: -1.0085e-010%
When DG6 is shifted, the RMS residual increases by: -4.4883e-012%

(b) Titration of 0.010 0M $Co(BF_4)_2$ with 0 to 3.1 equivalents of L^{bip} at 308 K.



Optimization Summary:
Data at 308 K
Non-negativity was enforced with truncation (not optimization).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): $\Delta G°_1$ = -166(2); $\Delta G°_2$ = -162(1); $\Delta G°_3$ = -154(1); $\Delta G°_4$ = -57.8(8);
$\Delta G°_5$ = -62.3(8); $\Delta G°_6$ = -6.2(3);
Equilibrium Restricted RMS Residual (7 chemical factors): 0.00078715
Unrestricted RMS Residual (7 mathematical factors): 0.00026202
Restricted Data Reconstruction (7 chemical factors): 97.9687%
Unrestricted Data Reconstruction (7 mathematical factors): 98.2729%
Remaining Error Imbedded in Absorbance Values: 0.00033348
R^2: 99.9813%

Estimating model sensitivity to DG values...

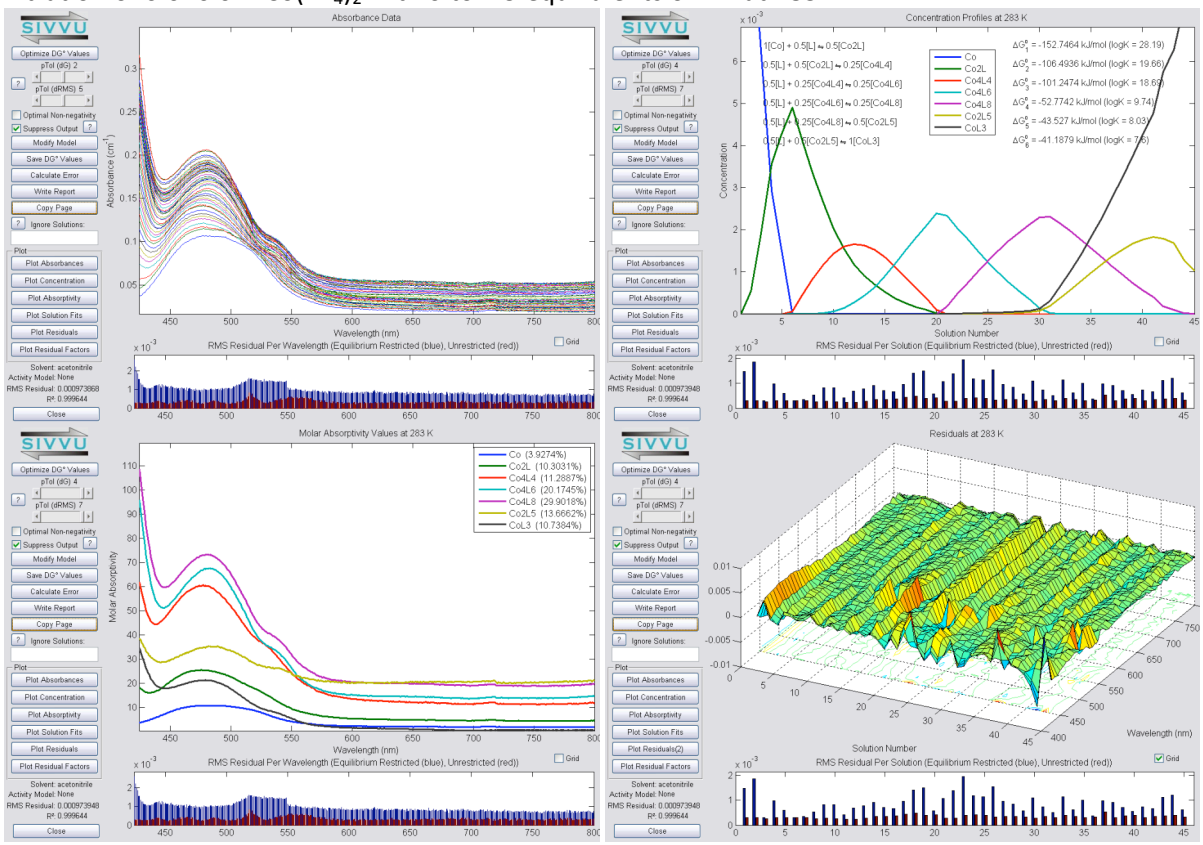
Each DG value is changed by 1 kJ/mol in both directions.
The resulting average change in RMS Residual corresponds to how
sensitive the model is to that particular DG value.

When DG1 is shifted, the RMS residual increases by: 0.023813%
When DG2 is shifted, the RMS residual increases by: 0.087707%
When DG3 is shifted, the RMS residual increases by: 0.050783%
When DG4 is shifted, the RMS residual increases by: 0.11596%
When DG5 is shifted, the RMS residual increases by: 0.11596%
When DG6 is shifted, the RMS residual increases by: 0.014084%

Then, each DG value is changed again, but now the others are allowed
to reoptimize. The resulting change in RMS Residual corresponds to how
independent that particular DG value is. Vanishingly small or negative values
indicate that only the difference between DG values is known accurately.

When DG1 is shifted, the RMS residual increases by: 2.1554e-009%
When DG2 is shifted, the RMS residual increases by: -5.852e-009%
When DG3 is shifted, the RMS residual increases by: 9.7575e-009%
When DG4 is shifted, the RMS residual increases by: 9.7845e-009%
When DG5 is shifted, the RMS residual increases by: 9.7867e-009%
When DG6 is shifted, the RMS residual increases by: 0.013326%

Titration of 0.010 0M $Co(BF_4)_2$ with 0 to 2.9 equivalents of L^{bip} at 283 K.



Optimization Summary:
Data at 283 K
Non-negativity was enforced with truncation (not optimization).
Activity Coefficients Model: None.
Species with Fixed Molar Absorptivity Curves: None.
Solutions ignored: None.
Optimized Values (kJ/mol): ΔG°_1 = -153(3); ΔG°_2 = -106.5(1); ΔG°_3 = -101.2(1);
ΔG°_4 = -52.8(5); ΔG°_5 = -43.5(1); ΔG°_6 = -41.2(1);
Equilibrium Restricted RMS Residual (7 chemical factors): 0.00097395
Unrestricted RMS Residual (7 mathematical factors): 0.00034412
Restricted Data Reconstruction (7 chemical factors): 97.7633%
Unrestricted Data Reconstruction (7 mathematical factors): 98.1881%
Remaining Error Imbedded in Absorbance Values: 0.00041802
R^2: 99.9644%

Estimating model sensitivity to DG values...
Each DG value is changed by 1 kJ/mol in both directions.
The resulting average change in RMS Residual corresponds to how sensitive the model is to that particular DG value.
When DG1 is shifted, the RMS residual increases by: 4.5722e-009%
When DG2 is shifted, the RMS residual increases by: 0.078127%
When DG3 is shifted, the RMS residual increases by: 0.078127%
When DG4 is shifted, the RMS residual increases by: 0.020215%
When DG5 is shifted, the RMS residual increases by: 3.9349%
When DG6 is shifted, the RMS residual increases by: 3.7672%

Then, each DG value is changed again, but now the others are allowed to reoptimize. The resulting change in RMS Residual corresponds to how independent that particular DG value is. Vanishingly small or negative values

indicate that only the difference between DG values is known accurately.
When DG1 is shifted, the RMS residual increases by: -1.1581e-008%
When DG2 is shifted, the RMS residual increases by: -1.644e-008%
When DG3 is shifted, the RMS residual increases by: -1.6616e-008%
When DG4 is shifted, the RMS residual increases by: -1.7767e-008%
When DG5 is shifted, the RMS residual increases by: -1.6674e-008%
When DG6 is shifted, the RMS residual increases by: -1.6973e-008%