Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

An S_4-Symmetric Mixed-Valent Decacopper Cage Comprised of [Cu^{II}(*L*-S_2N_2)] Complexes Bridged by $Cu^{I}(MeCN)_n$ (*n* = 1 or 2) Cations

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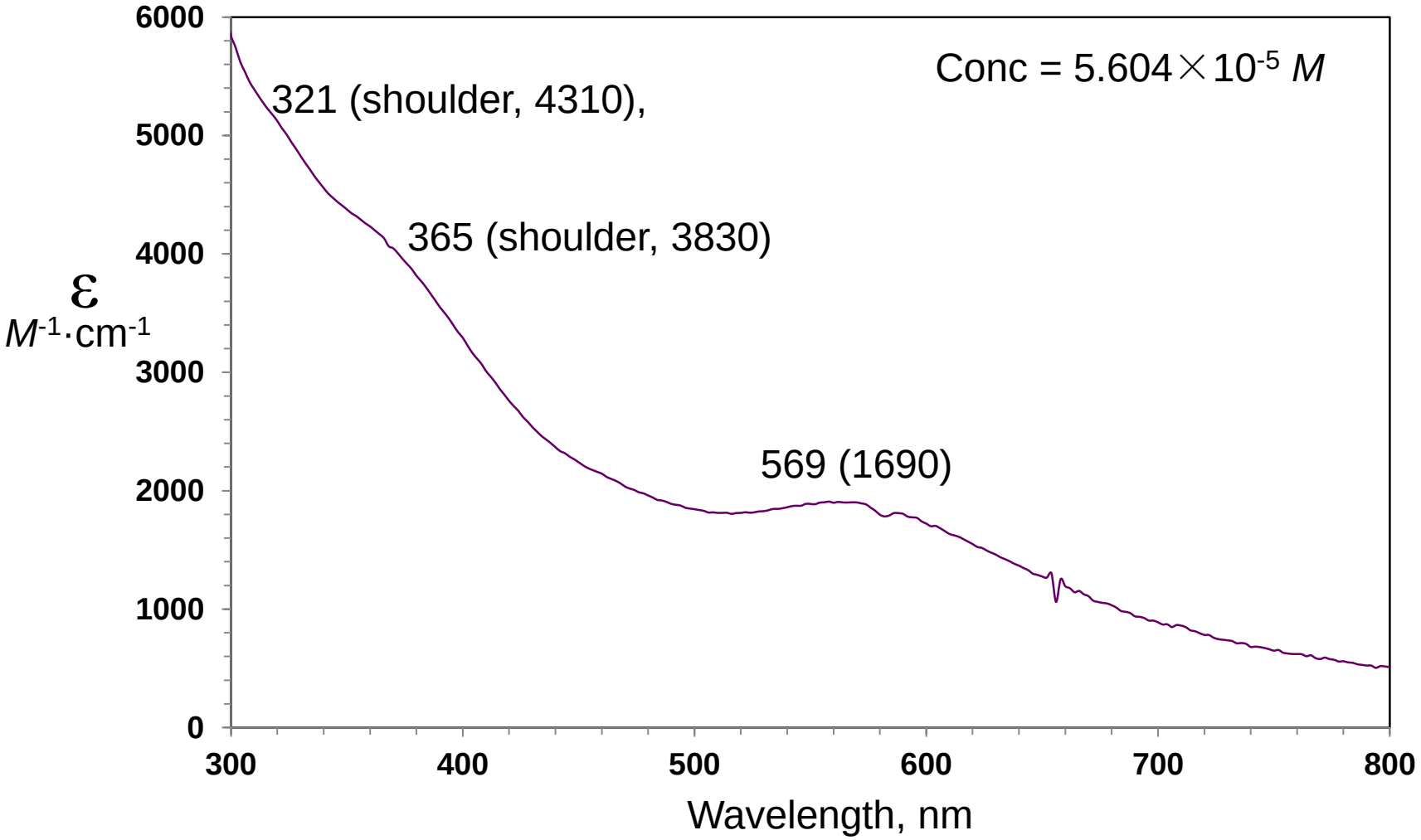
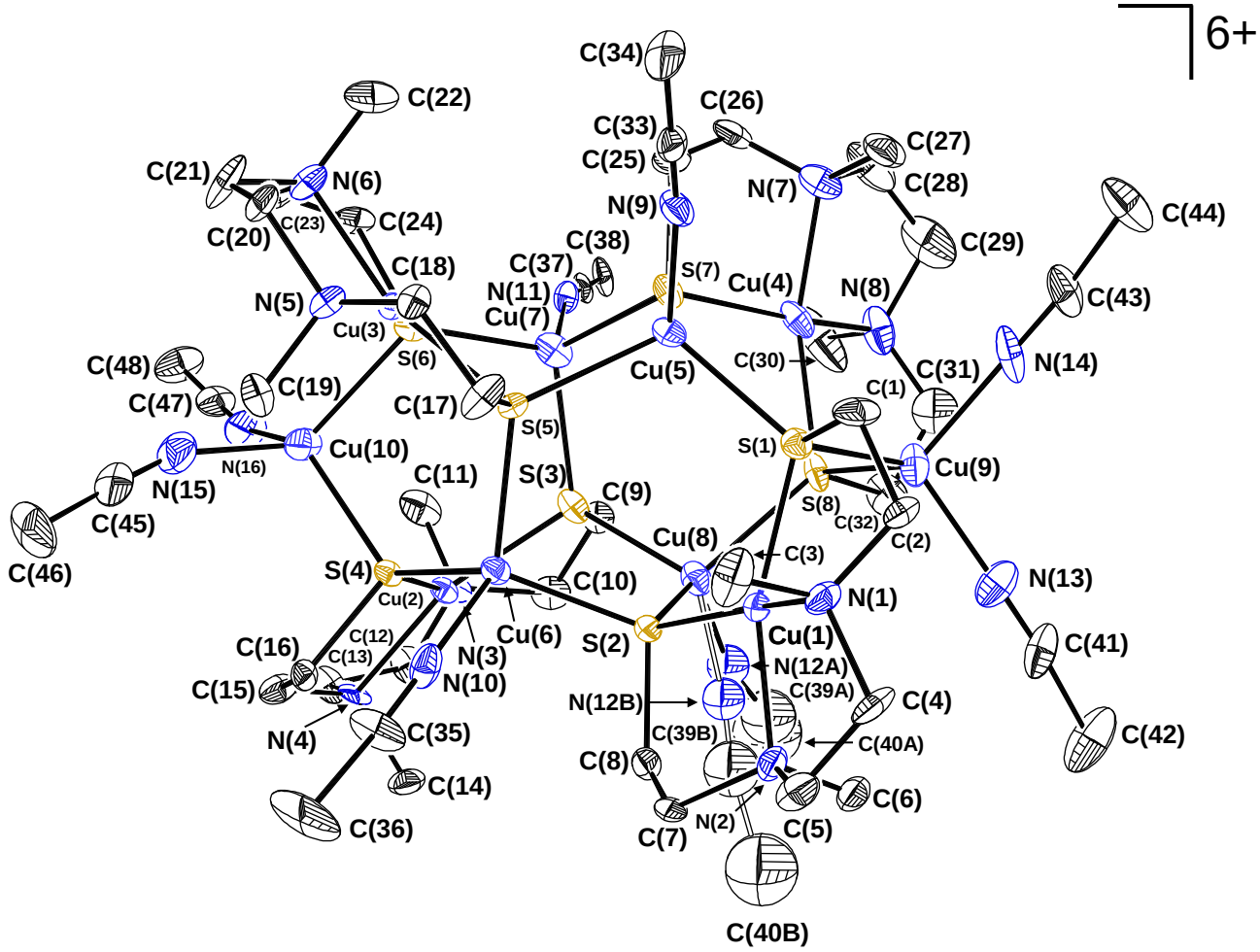
UV-vis Spectrum in MeCN of $[(Cu^{II}(\mathit{L}\text{-}N_2S_2))_4(\mu_2\text{-}Cu^{I}(MeCN)_2)_2(\mu_3\text{-}Cu^{I}(MeCN))_4][BF_4]_6\cdot 2.25MeCN$

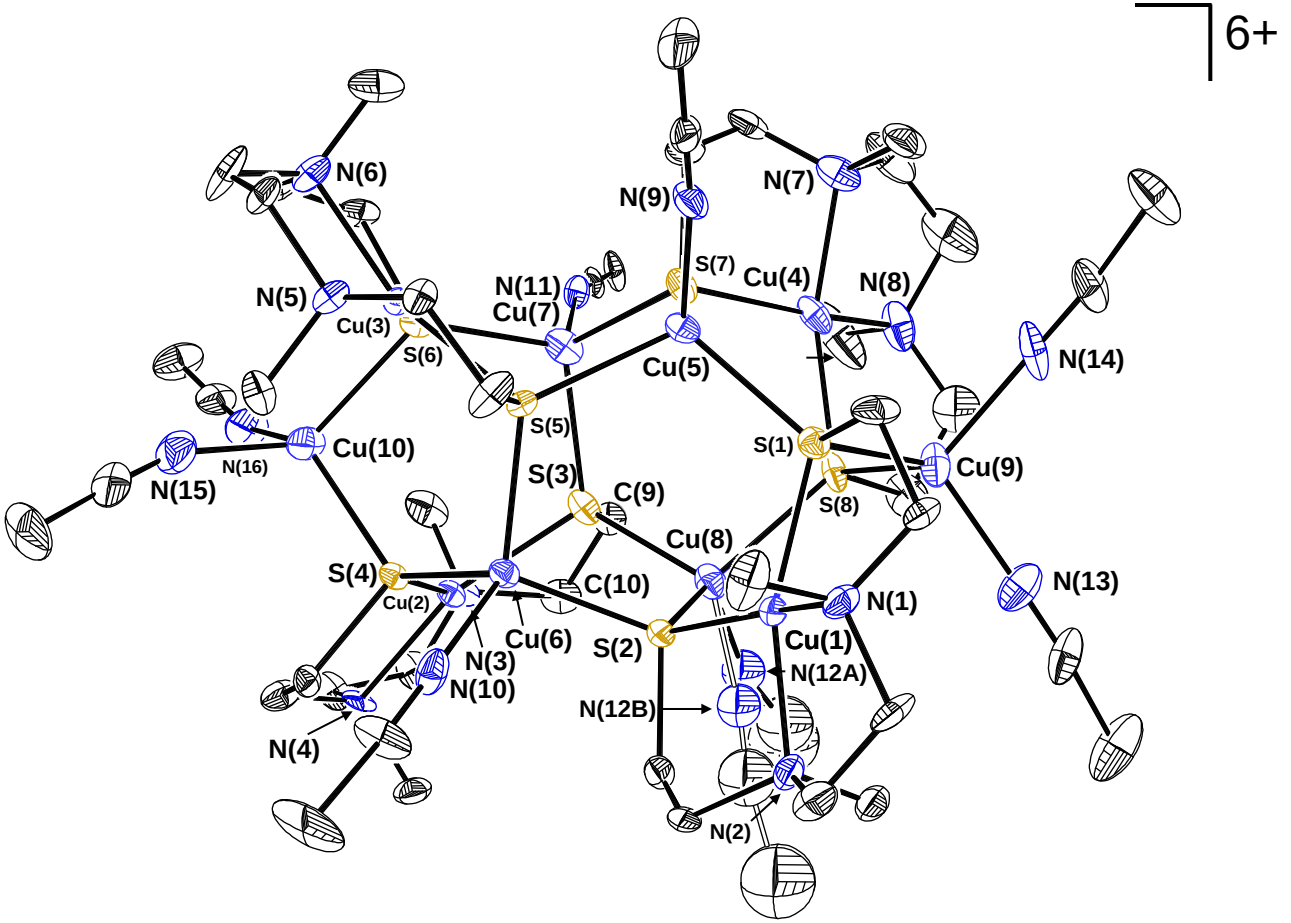


Atom Labeling for Cation 1 of $[Cu_{10}(S(CH_2)_2N(Me)CH_2-)_2(MeCN)_8][BF_4]_6\cdot(MeCN)_{2.25}$



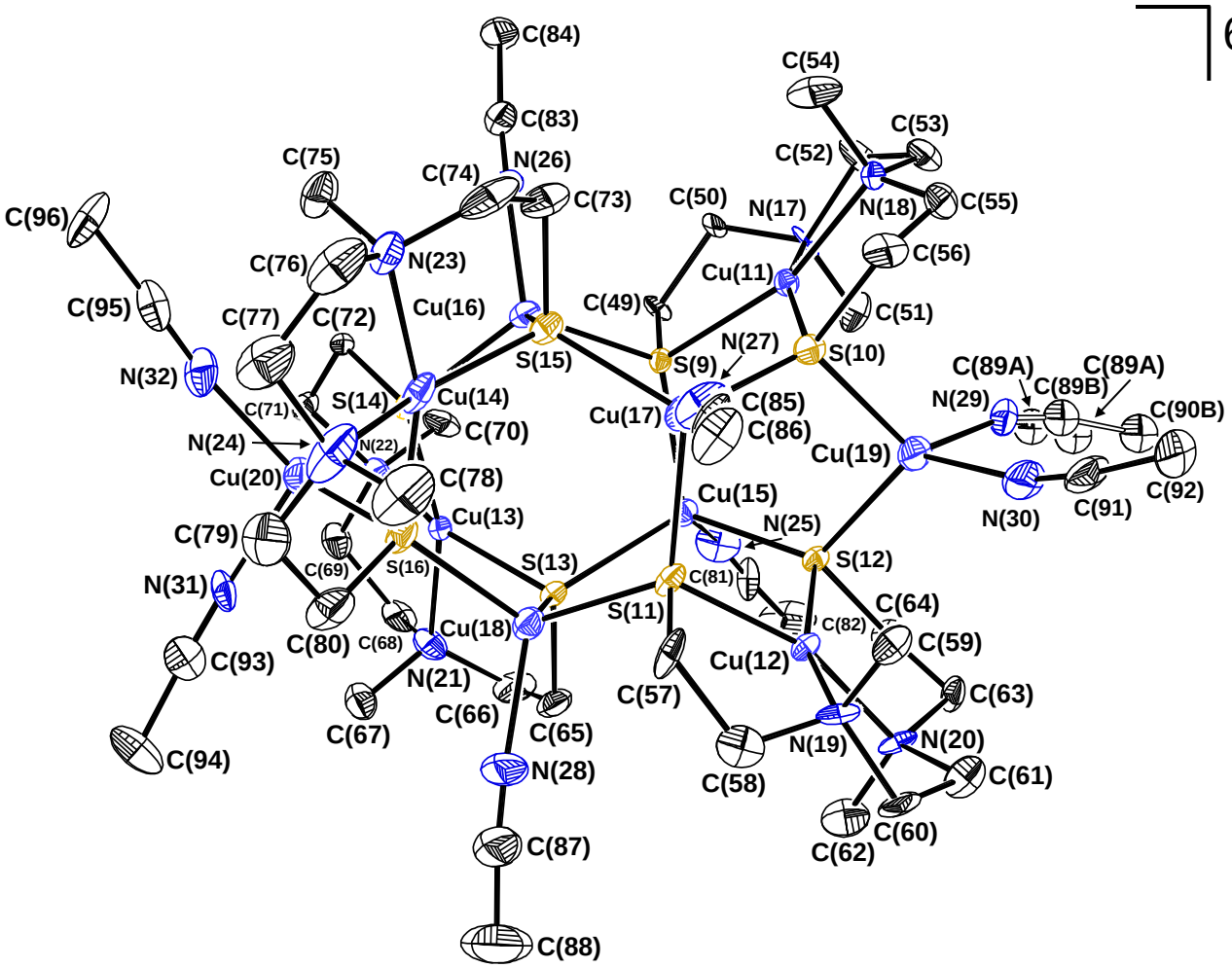
Thermal ellipsoid plot is drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

Partial Atom Labeling for Cation 1 of $[Cu_{10}(S(CH_2)_2N(Me)CH_2-)_2(MeCN)_8][BF_4]_6\cdot(MeCN)_{2.25}$



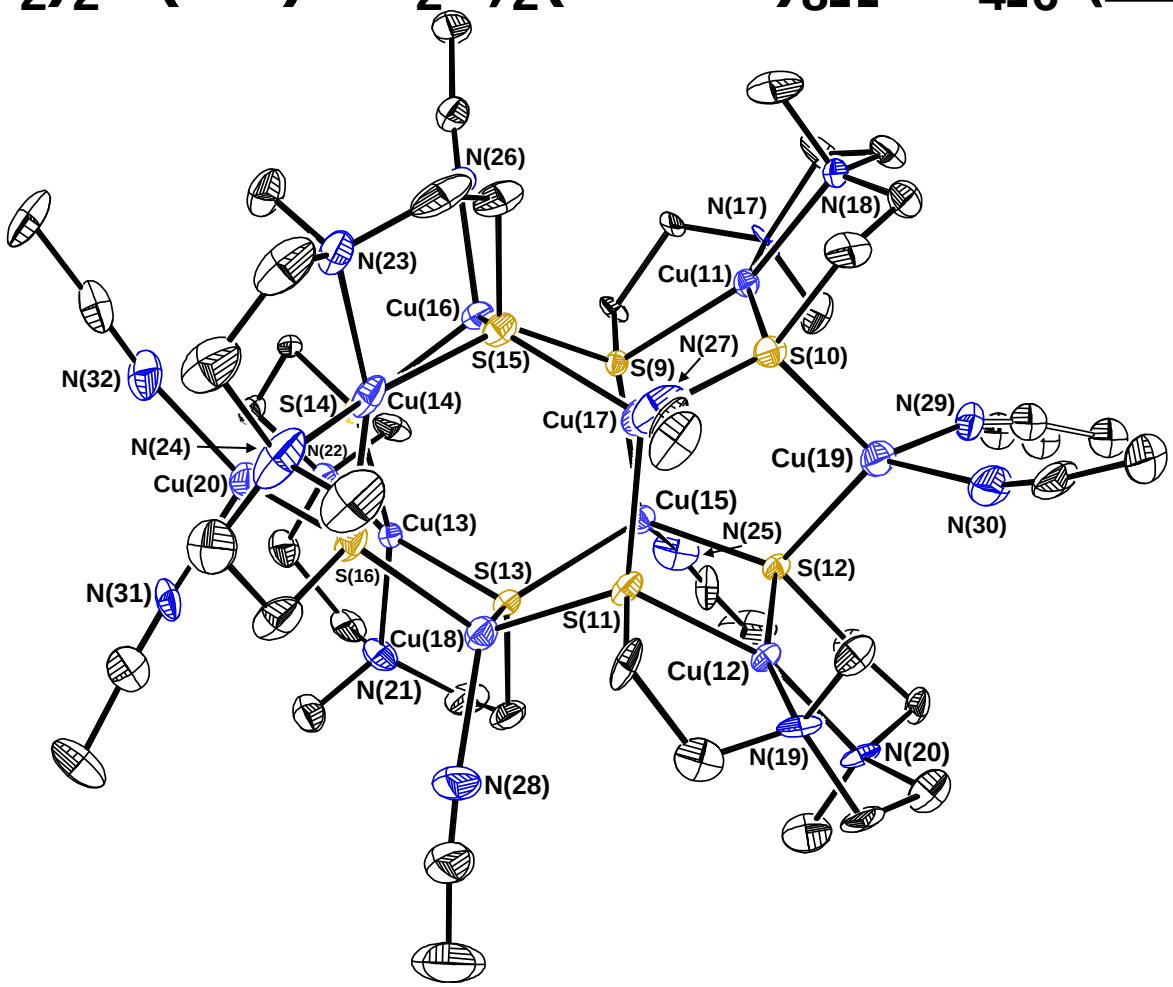
Thermal ellipsoid plot is drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

Atom Labeling for Cation 2 of $[Cu_{10}(S(CH_2)_2N(Me)CH_2-)_2(MeCN)_8][BF_4]_6\cdot(MeCN)_{2.25}$



Thermal ellipsoid plot is drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

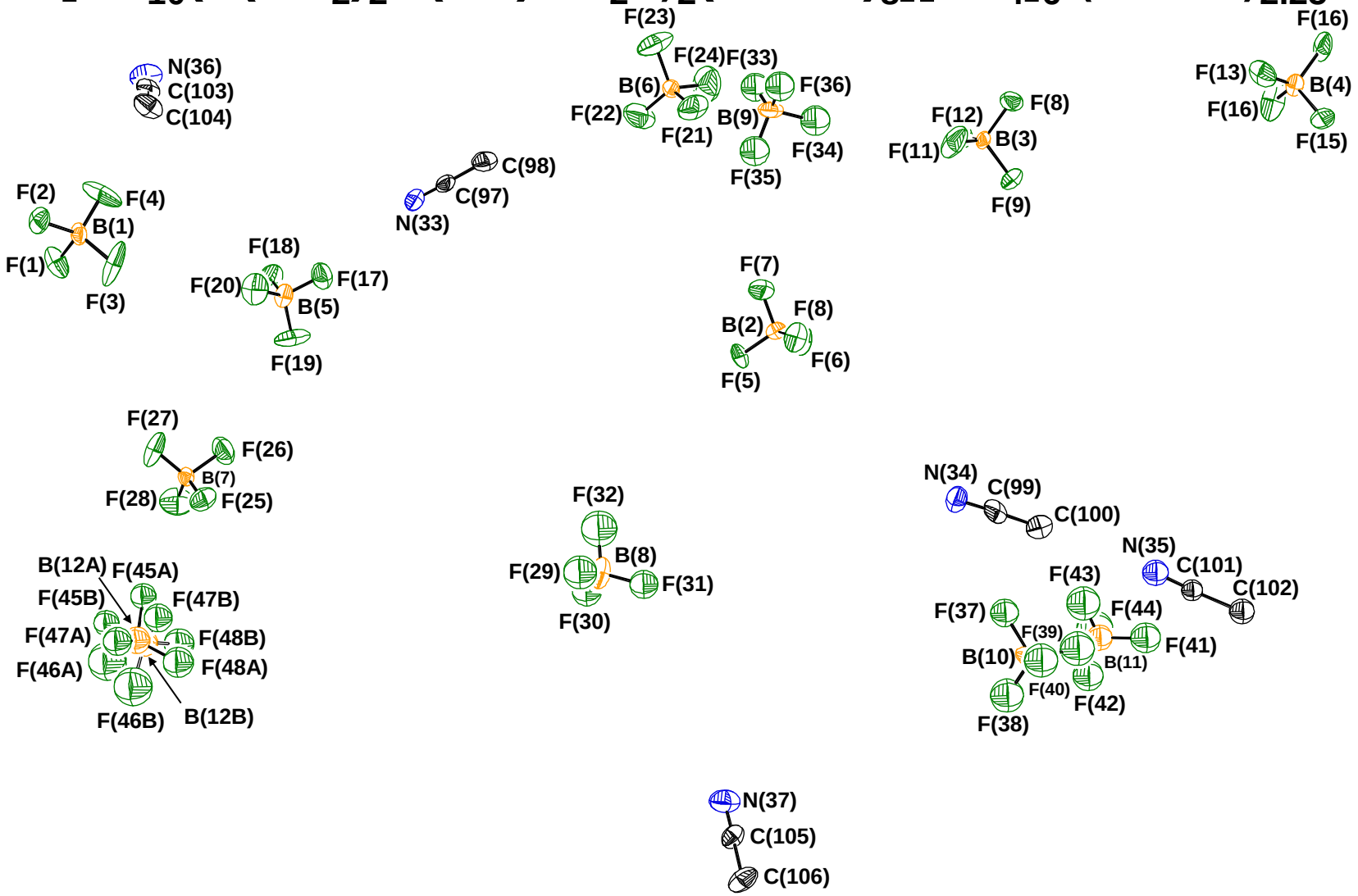
Partial Atom Labeling for Cation 2 of $[Cu_{10}(S(CH_2)_2N(Me)CH_2-)_2(MeCN)_8][BF_4]_6\cdot(MeCN)_{2.25}$



Thermal ellipsoid plot is drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

Atom Labeling for $[BF_4]^{1-}$ Anions and Interstitial MeCN

$[Cu_{10}(S(CH_2)_2N(Me)CH_2-)_2(MeCN)_8][BF_4]_6\cdot(MeCN)_{2.25}$



Thermal ellipsoid plot is drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.