Supporting Information for

# Structural Tuning of Ligand-Based Two-Electron Intervalence Charge Transfer 

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## Experimental Procedures

Materials. All compounds were handled, reactions were performed, and analytical samples were prepared in inert atmosphere using standard Schlenk, dry-box and vacuum-line techniques. Solvents were purchased from VWR Scientific Products and purified using a Braun solvent purification system or using standard solvent purification techniques. ${ }^{1}$ Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, dried and distilled by procedures similar to those used for non-isotopically enriched solvents. Technical grade ferrocenium tetrafluoroborate $\left(\mathrm{FcBF}_{4}\right)$ was purchased from Aldrich, dissolved in acetonitrile and dried over calcium hydride at room temperature; the solvent was degassed and the solid was precipitated with diethylether, collected by filtration and dried in vacuum. Octamethylporphyrinogen, $\mathrm{LH}_{4}$, was prepared according to standard procedures. ${ }^{2}$ Other reagents were purchased from Aldrich, Alfa Aesar or Strem Chemicals and used as received. Elemental analyses were conducted at H. Kolbe Mikroanalytisches Laboratorium (Mühlheim a. d. Ruhr, Germany).

Synthesis of $\mathbf{L i}_{\mathbf{2}}$ (1,4-dioxane) $)_{5}[\mathbf{L M g}] . \mathrm{LH}_{4}(10.0 \mathrm{~g}, 23.3 \mathrm{mmol})$ was dissolved in 400 mL of $1,4-$ dioxane and 23.5 mL of a $2.0-\mathrm{M} \mathrm{Et}_{2} \mathrm{O}$ solution ( 46.7 mmol , 2 equiv) of ethylmagnesium chloride was added. The resulting white suspension was refluxed overnight, the mixture was cooled down to room temperature and filtered and butyllithium $(23.5 \mathrm{~mL}$ of a $2.0-\mathrm{M}$ pentane solution, 46.7 mmol, 2 equiv) was added to the filtrate and the mixture was again refluxed overnight. The mixture was then cooled to room temperature and the product was collected by filtration and dried. Yield: $10.98 \mathrm{~g}(50 \%)$. The solid was then recrystallized from 1,4-dioxane. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=5.66(\mathrm{~s}, 8 \mathrm{H}$, pyrrole), $3.62(\mathrm{~s}, 40 \mathrm{H}$, dioxane), 1.49 ( $\mathrm{s}, 24 \mathrm{H}, \mathrm{Me}$ ). Anal. Calcd for $\mathrm{C}_{48} \mathrm{H}_{72} \mathrm{Li}_{2} \mathrm{MgN}_{4} \mathrm{O}_{10}$ : C, 63.82; H, 8.04; N, 6.21. Found: C, 63.73; H, 7.94; N, 6.15.

Synthesis of $\left[\mathbf{L}^{\mathbf{\Delta 4}} \mathbf{M g}\right]\left(\mathbf{B F}_{4}\right)_{2}$. Two separate $10-\mathrm{mL}$ MeCN solutions of $\operatorname{LMgLi}_{2}(\operatorname{diox})_{5}(0.48 \mathrm{~g}$, $0.53 \mathrm{mmol})$ and $\mathrm{FcBF}_{4}(0.60 \mathrm{~g}, 2.11 \mathrm{mmol}, 4$ equiv.) were prepared. The former was added dropwise to the latter, and the combined green solution was evaporated and dried in vacuum.

The solid residue was triturated in 200 mL of boiling $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and the resulting suspension was filtered. The filtrate was evaporated and dried, then triturated in 200 mL hexanes, filtered and dried again. The off-white (greenish) powder was recrystallized from $\mathrm{CH}_{2} \mathrm{Cl}_{2}(80 \mathrm{~mL}) /$ hexanes ( 30 mL ). Yield: $0.09 \mathrm{~g}(30 \%) .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=7.88(\mathrm{~d}, 5 \mathrm{~Hz}, 4 \mathrm{H}$, pyrrole), $6.96(\mathrm{~d}, 5 \mathrm{~Hz}, 4 \mathrm{H}$, pyrrole), $2.01(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Me}), 1.86(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Me}), 1.84(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Me}), 1.80(\mathrm{~s}, 6 \mathrm{H}$, Me). Anal. Calcd for $\mathrm{C}_{28} \mathrm{H}_{32} \mathrm{~N}_{4} \mathrm{MgB}_{2} \mathrm{~F}_{8}$ : C, 54.00 ; H, 5.18; N, 9.00. Found: C, 53.73; H, 5.24; N, 8.79.

Synthesis of $\left[\mathbf{L}^{\mathbf{4}} \mathbf{M g}\right] . \operatorname{Li}_{2}(\text { diox })_{5}[\mathrm{LMg}](121 \mathrm{mg}, 0.134 \mathrm{mmol})$ was dissolved in 3 mL of MeCN and added to powdered $\left[\mathrm{L}^{\Delta \Lambda} \mathrm{Mg}\right]\left(\mathrm{BF}_{4}\right)_{2}(76 \mathrm{mg}, 0.134 \mathrm{mmol})$. The resulting vermilion red solution was evaporated. The remaining solid residue was triturated in 3 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and the white salt was filtered off and the filtrate evaporated and dried to give $120 \mathrm{mg}(100 \%)$ of crude material. Single crystals of X-ray quality were grown by vapor diffusion of toluene into a concentrated $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of the product that was spiked with MeCN ; diffraction data showed that the acetonitrile adduct $\left[\mathrm{L}^{\Delta} \mathrm{Mg}(\mathrm{NCMe})\right] \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ was obtained.

Preparation of activated calcium. Calcium iodide ( $12.03 \mathrm{~g}, 40.93 \mathrm{mmol}$ ), naphthalene (10.49 $\mathrm{g}, 81.85 \mathrm{mmol}, 2$ equiv.) and lithium metal $(0.568 \mathrm{~g}, 81.85 \mathrm{mmol}, 2$ equiv) were mixed in 100 mL THF and the mixture was stirred at room temperature overnight. The black suspension was filtered and dried under vacuum on the frit at room temperature. The solid was transferred to a high-vacuum flask and further dried overnight under $10 \mu$ Torr at $140^{\circ} \mathrm{C}$. Yield: $4.99 \mathrm{~g}(72 \%)$ of black $\mathrm{Ca}\left(\mathrm{C}_{10} \mathrm{H}_{8}\right)_{0.98}$. Anal. Calcd for $\mathrm{C}_{9.80} \mathrm{H}_{7.84} \mathrm{Ca}: \mathrm{C}, 71.07$; H, 4.78; Ca, 24.15. Found: C, 71.08; H, 4.71; Ca, 24.37.

Synthesis of $\mathbf{L C a}_{\mathbf{2}}(\mathbf{N C M e})_{4}$. Activated calcium $(1.94 \mathrm{~g}, 11.53 \mathrm{mmol})$ and $\mathrm{LH}_{4}(2.47 \mathrm{~g}, 5.77$ mmol, 0.5 equiv.) were mixed in THF and refluxed overnight. The colorless solution was cooled to room temperature, then cooled further to $-80^{\circ} \mathrm{C}$ where the temperature of the solution was maintained for 2 hr . The white precipitate was filtered cold, dried, recrystallized from toluene
$(100 \mathrm{~mL}) / \mathrm{MeCN}(200 \mathrm{~mL})$ and dried in vacuum. Yield: $1.02 \mathrm{~g}(27 \%) .{ }^{1} \mathrm{H}$ NMR ( 500 MHz , THF- $\mathrm{d}_{8}$ ): $\delta=5.89(\mathrm{~s}, 8 \mathrm{H}$, pyrrole $), 1.95(\mathrm{~s}, 12 \mathrm{H}, \mathrm{MeCN}), 1.31(\mathrm{~s}, 24 \mathrm{H}, \mathrm{Me})$.

Synthesis of $\left[\mathbf{L}^{\Delta \Delta} \mathbf{C a}\right]\left(\mathbf{B F}_{4}\right)_{\mathbf{2}}$. A 5-mL toluene suspension of $\mathrm{LCa}_{2}(\mathrm{NCMe})_{4}(0.48 \mathrm{~g}, 0.71 \mathrm{mmol})$ was added dropwise to a $20-\mathrm{mL} \mathrm{MeCN}$ solution of $\mathrm{FcBF}_{4}(0.62 \mathrm{~g}, 2.28 \mathrm{mmol}, 4$ equiv). The resulting green solution was evaporated and dried under vacuum. The solid was triturated in 30 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ for 20 min ., filtered, and resuspended in 300 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, which was then brought to reflux. The warm suspension was filtered and the product was precipitated from the filtrate by dropwise addition of 100 mL of hexanes. The white powder was filtered and dried in vacuum. Yield: $0.13 \mathrm{~g}(37 \%) .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta=7.73(\mathrm{~d}, 5 \mathrm{~Hz}, 4 \mathrm{H}$, pyrrole), $6.81(\mathrm{~d}, 5 \mathrm{~Hz}, 4 \mathrm{H}$, pyrrole), $2.00(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Me}), 1.87(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Me}), 1.80(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Me}), 1.79(\mathrm{~s}, 6 \mathrm{H}$, Me). Anal. Calcd for [ $\left.\mathrm{L}^{\Delta \Delta} \mathrm{Ca}\right]\left(\mathrm{BF}_{4}\right)_{2} \cdot 0.3 \mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{C}_{28.3} \mathrm{H}_{32.6} \mathrm{~N}_{4} \mathrm{CaB}_{2} \mathrm{~F}_{8} \mathrm{Cl}_{0.6}: \mathrm{C}, 51.19$; $\mathrm{H}, 4.95$; N , 8.44; Ca, 6.02. Found: C, 51.54; H, 4.82; N, 8.30; Ca, 6.08.

Synthesis of $\left[\mathbf{L}^{\mathbf{U}} \mathbf{C a}\right]$. A $5-\mathrm{mL} \mathrm{MeCN}$ suspension of $\left[\mathrm{L}^{\Delta \Delta} \mathrm{Ca}\right]\left(\mathrm{BF}_{4}\right)_{2}(90 \mathrm{mg}, 0.13 \mathrm{mmol})$ was added to a $5-\mathrm{mL} \mathrm{MeCN}$ solution of $\mathrm{LCa}_{2}(\mathrm{NCMe})_{4}(86 \mathrm{mg}, 0.13 \mathrm{mmol})$ under stirring. The brown mixture was stirred for 10 min . at room temperature, then evaporated and dried in vacuum. The solid residue was triturated in $3 \mathrm{mLCH} \mathrm{Cl}_{2}$ and filtered, then the filtrate was evaporated and dried. The compound decomposes in solution, but is reasonably stable as a solid for a few days. Its decomposition was monitored by UV-vis in dilute solution at room temperature, and under those conditions we observed a marked bleach of its spectrum overnight. Its solid-state stability is better, however after several days in the glovebox. In a regular vial (capped but not Teflonlined) the solid was found to be partly decomposed. Cooling it to $-30^{\circ} \mathrm{C}$ or even $-80^{\circ} \mathrm{C}$ only marginally improved its stability. This instability prevented us from obtaining X-ray quality crystals, which in our hands need to be grown extremely slowly for all of our metalloporphyrinogens (a week to several weeks). For purification, the recrystallization was performed quickly (carried out over a few hours) by liquid-liquid diffusion of pentane into a concentrated $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution to yield a microcrystalline powder. Yield: $110 \mathrm{mg}(88 \%)$. Anal.

Calcd for $\left[\mathrm{L}^{\Delta} \mathrm{Ca}\right] \cdot 0.18 \mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{C}_{28.18} \mathrm{H}_{32.36} \mathrm{~N}_{4} \mathrm{CaCl}_{0.36}: \mathrm{C}, 70.55 ; \mathrm{H}, 6.80 ; \mathrm{N}, 11.69$; Ca, 8.34. Found: C, 70.88; H, 6.46; N, 11.25; Ca, 8.26.

X-ray Crystal Structure of $\left[\mathbf{L}^{\mathbf{4}} \mathbf{M g}\left(\mathbf{C H}_{\mathbf{3}} \mathbf{C N}\right)\right] \cdot \mathbf{C H}_{\mathbf{2}} \mathbf{C l}_{\mathbf{2}}$. A bright vermilion red crystal of $0.44 \times$ $0.21 \times 0.06 \mathrm{~mm}^{3}$ dimension was coated with Paratone N oil and mounted on a glass fiber. X-ray diffraction data were collected at $-80^{\circ} \mathrm{C}$ on a Siemens CCD diffractometer, using the Mo $\mathrm{K} \alpha$ radiation, selected by a graphite monochromator. The data were integrated to $h k \ell$-intensity and the final unit cell calculated using the SAINT v.4.050 program from Siemens. Solution and refinement were performed with the SHELXTL v.5.03 suite of programs developed by G. M. Sheldrick and Siemens Industrial Automation, 1995. The structure was solved by direct methods; the least-squares refinement converged normally (with hydrogen atoms placed at calculated positions using a standard riding model and refined isotropically).

Physical Measurements. UV-vis solution absorption spectra were recorded on a Cary-17 spectrophotometer modified by On-Line Instrument Systems (OLIS) to include computer control, or a Spectral Instruments 440 Model spectrophotometer. NMR spectra were recorded at the MIT Department of Chemistry Instrumentation Facility (DCIF) on a Varian Inova-500 spectrometer at $20^{\circ} \mathrm{C}$.

Computational Methods. A single-point (SP) density functional theoretical (DFT) computation was performed on the atomic coordinates of the crystal structure using the Amsterdam Density Functional (ADF2002.02) program ${ }^{3,4}$ on a home-built Linux cluster comprising sixty Intel processors organized in groups of twelve running in parallel. The generalized gradient approximation was used as implemented in ADF by the Becke- 88 functional for exchange, ${ }^{5}$ and the Perdew-Wang-91 functional for correlation. ${ }^{6}$ A basis set of triple- $\zeta$ Slater-type functions augmented by a polarization set (TZP) was used for Mg and N atoms and double- $\zeta$ with polarization (DZP) for other atoms, with frozen core approximation. Orbitals were visualized using the Windows or Linux version of the Molekel software. ${ }^{7,8}$

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Table S1. Crystal data, structure solution and refinement for $\left[\mathrm{L}^{\Delta} \mathrm{Mg}\left(\mathrm{CH}_{3} \mathrm{CN}\right)\right] \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

| identification code | 00325 t |
| :--- | :--- |
| empirical formula | $\mathrm{C}_{31} \mathrm{H}_{37} \mathrm{Cl}_{2} \mathrm{MgN}_{5}$ |
| formula weight | 574.87 |
| $T(\mathrm{~K})$ | $193(2)$ |
| $\lambda(\AA)$ | 0.71073 |
| crystal system | Triclinic |
| space group | $P \overline{1}$ |
| $a(\AA)$ | $10.4274(7)$ |
| $b(\AA)$ | $10.6231(7)$ |
| $c(\AA)$ | $14.3549(10)$ |
| $\alpha($ deg $)$ | $81.9710(10)$ |
| $\beta($ deg $)$ | $85.0730(10)$ |
| $\gamma($ deg $)$ | $73.5010(10)$ |
| $V\left(\AA^{3}\right)$ | $1507.90(18)$ |
| $Z$ | 2 |
| $\rho_{\text {calcd }}\left(\mathrm{g}\right.$ cm $\left.{ }^{-3}\right)$ | 1.266 |
| crystal size $\left(\mathrm{mm}{ }^{3}\right)$ | $0.44 \times 0.21 \times 0.08$ |
| abs coeff $\left(\mathrm{mm}{ }^{-1}\right)$ | 0.265 |
| $F(000)$ | 608 |
| $\theta$ range for data collection | 2.01 to $23.29^{\circ}$ |
| limiting indices | $-11 \leq h \leq 10,-11 \leq k \leq 11,-15 \leq \ell \leq 15$ |
| no. of reflns collcd | 7845 |
| no. of ind reflns $\left(R_{\text {int }}\right)$ | $4327(0.0504)$ |
| completeness to $\theta=23.25^{\circ}$ | $99.7 \%$ |
| absorption corr | none |
| refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| data / restraints $/$ parameters | $4327 / 0 / 362$ |
| $R 1,{ }^{\text {a }} w R 2^{\mathrm{b}}[I>2 \sigma]$ | $0.0928,0.2700$ |
| $R 1,{ }^{\text {a }} w R 2^{\mathrm{b}}($ all data $)$ | $0.1104,0.2899$ |
| GOF $F^{\mathrm{c}}$ on $F^{2}$ | 1.028 |
| extinction coefficient | $0.0000(4)$ |
| largest diff. peak and hole | 0.690 and $-1.222 \mathrm{e} \AA^{-3}$ |

${ }^{a} R 1=\Sigma| | F_{\mathrm{o}}-\left|F_{\mathrm{c}}\right||/ \Sigma| F_{\mathrm{o}} \mid . \quad{ }^{b} \mathrm{w} R 2=\left(\Sigma\left(w\left(F_{\mathrm{o}}{ }^{2}-F_{\mathrm{c}}{ }^{2}\right)^{2}\right) / \Sigma\left(w\left(F_{\mathrm{o}}{ }^{2}\right)^{2}\right)\right)^{1 / 2} .{ }^{c} \mathrm{GOF}=\left(\Sigma w\left(F_{\mathrm{o}}{ }^{2}-\right.\right.$ $\left.\left.F_{\mathrm{c}}^{2}\right)^{2} /(n-p)\right)^{1 / 2}$ where $n$ is the number of data and $p$ is the number of parameters refined.


Figure S1. Atomic numbering scheme for the crystal structure of $\left[\mathrm{L}^{\Delta} \mathrm{Mg}\left(\mathrm{CH}_{3} \mathrm{CN}\right)\right] \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$. The dichloromethane solvent molecule, which is not shown, is labeled with atoms $\mathrm{C}(31), \mathrm{Cl}(1)$ and $\mathrm{Cl}(2)$.

Table S2. Atomic coordinates $\left(\times 10^{4}\right)$ and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\left[\mathrm{L}^{4} \mathrm{Mg}\left(\mathrm{CH}_{3} \mathrm{CN}\right)\right] \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

| Atom | x | y | z | $\mathrm{U}_{\mathrm{eq}}{ }^{\mathrm{a}}$ |
| :--- | ---: | ---: | ---: | ---: |
| $\mathrm{Mg}(1)$ | $816(2)$ | $4450(2)$ | $7424(1)$ | $22(1)$ |
| $\mathrm{N}(1)$ | $496(4)$ | $6476(4)$ | $6721(3)$ | $25(1)$ |
| $\mathrm{N}(3)$ | $916(4)$ | $2489(4)$ | $7342(3)$ | $24(1)$ |
| $\mathrm{N}(4)$ | $-1215(4)$ | $4936(4)$ | $7819(3)$ | $25(1)$ |
| $\mathrm{N}(2)$ | $2362(4)$ | $4281(4)$ | $6275(3)$ | $25(1)$ |
| $\mathrm{N}(5)$ | $1902(4)$ | $4457(4)$ | $8618(3)$ | $33(1)$ |
| $\mathrm{C}(18)$ | $-141(5)$ | $1948(5)$ | $7584(3)$ | $26(1)$ |
| $\mathrm{C}(15)$ | $1837(5)$ | $1604(5)$ | $6820(3)$ | $25(1)$ |
| $\mathrm{C}(25)$ | $-2120(5)$ | $6156(5)$ | $7654(3)$ | $27(1)$ |
| $\mathrm{C}(11)$ | $2827(5)$ | $3214(5)$ | $5866(3)$ | $24(1)$ |
| $\mathrm{C}(22)$ | $-1947(5)$ | $4028(5)$ | $7942(3)$ | $24(1)$ |
| $\mathrm{C}(5)$ | $2649(5)$ | $6560(5)$ | $5757(4)$ | $31(1)$ |
| $\mathrm{C}(12)$ | $3150(5)$ | $1867(5)$ | $6442(3)$ | $28(1)$ |
| $\mathrm{C}(8)$ | $2215(5)$ | $5378(5)$ | $5538(3)$ | $26(1)$ |
| $\mathrm{C}(19)$ | $-1292(5)$ | $2560(5)$ | $8245(3)$ | $29(1)$ |
| $\mathrm{C}(4)$ | $1154(5)$ | $6658(5)$ | $5806(3)$ | $27(1)$ |
| $\mathrm{C}(3)$ | $207(5)$ | $7675(5)$ | $5220(4)$ | $33(1)$ |
| $\mathrm{C}(1)$ | $-668(5)$ | $7351(5)$ | $6697(3)$ | $26(1)$ |
| $\mathrm{C}(29)$ | $2564(6)$ | $4425(6)$ | $9202(4)$ | $35(1)$ |
| $\mathrm{C}(26)$ | $-1657(5)$ | $7413(5)$ | $7536(4)$ | $31(1)$ |
| $\mathrm{C}(9)$ | $2509(5)$ | $4848(5)$ | $4642(4)$ | $32(1)$ |
| $\mathrm{C}(16)$ | $1366(5)$ | $538(5)$ | $6731(4)$ | $30(1)$ |
| $\mathrm{C}(10)$ | $2934(5)$ | $3529(6)$ | $4835(4)$ | $32(1)$ |
| $\mathrm{C}(27)$ | $-969(6)$ | $7486(5)$ | $8429(4)$ | $36(1)$ |
| $\mathrm{C}(2)$ | $-864(5)$ | $8132(5)$ | $5775(4)$ | $34(1)$ |
| $\mathrm{C}(20)$ | $-745(6)$ | $2432(6)$ | $9235(4)$ | $38(1)$ |
| $\mathrm{C}(23)$ | $-3297(5)$ | $4675(5)$ | $7839(3)$ | $28(1)$ |
| $\mathrm{C}(13)$ | $4044(5)$ | $1883(5)$ | $7240(4)$ | $35(1)$ |
| $\mathrm{C}(14)$ | $3943(5)$ | $794(5)$ | $5836(4)$ | $35(1)$ |
| $\mathrm{C}(17)$ | $110(5)$ | $749(5)$ | $7221(4)$ | $31(1)$ |
| $\mathrm{C}(24)$ | $-3409(5)$ | $6031(5)$ | $7654(3)$ | $28(1)$ |
| $\mathrm{C}(28)$ | $-2865(5)$ | $8643(5)$ | $7386(4)$ | $39(1)$ |
| $\mathrm{C}(21)$ | $-2353(6)$ | $1816(6)$ | $8324(4)$ | $39(1)$ |
| $\mathrm{C}(6)$ | $3366(5)$ | $6452(6)$ | $6646(4)$ | $38(1)$ |
| $\mathrm{C}(7)$ | $3155(6)$ | $7354(6)$ | $4912(4)$ | $40(1)$ |
| $\mathrm{C}(30)$ | $3428(8)$ | $4381(9)$ | $9952(5)$ | $73(2)$ |
| $\mathrm{Cl}(2)$ | $3401(7)$ | $10525(6)$ | $9676(3)$ | $206(2)$ |
| $\mathrm{C}(31)$ | $2518(9)$ | $9830(10)$ | $9083(6)$ | $84(3)$ |
| $\mathrm{Cl}(1)$ | $3575(5)$ | $8234(4)$ | $8781(3)$ | $160(2)$ |
|  |  |  |  |  |
|  |  |  |  |  |

[^0]Table S3. Bond lengths (in $\AA$ ) for $\left[\mathrm{L}^{\Delta} \mathrm{Mg}\left(\mathrm{CH}_{3} \mathrm{CN}\right)\right] \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

| Bond | Distance | Bond | Distance |
| :---: | :---: | ---: | :---: |
| $\mathrm{Mg}(1)-\mathrm{N}(3)$ | $2.076(4)$ | $\mathrm{C}(22)-\mathrm{C}(19)$ | $1.530(7)$ |
| $\mathrm{Mg}(1)-\mathrm{N}(4)$ | $2.080(4)$ | $\mathrm{C}(5)-\mathrm{C}(6)$ | $1.508(7)$ |
| $\mathrm{Mg}(1)-\mathrm{N}(5)$ | $2.136(5)$ | $\mathrm{C}(5)-\mathrm{C}(7)$ | $1.523(7)$ |
| $\mathrm{Mg}(1)-\mathrm{N}(1)$ | $2.193(4)$ | $\mathrm{C}(5)-\mathrm{C}(8)$ | $1.528(7)$ |
| $\mathrm{Mg}(1)-\mathrm{N}(2)$ | $2.194(4)$ | $\mathrm{C}(5)-\mathrm{C}(4)$ | $1.529(7)$ |
| $\mathrm{N}(1)-\mathrm{C}(1)$ | $1.302(6)$ | $\mathrm{C}(12)-\mathrm{C}(14)$ | $1.536(7)$ |
| $\mathrm{N}(1)-\mathrm{C}(4)$ | $1.443(6)$ | $\mathrm{C}(12)-\mathrm{C}(13)$ | $1.543(7)$ |
| $\mathrm{N}(3)-\mathrm{C}(18)$ | $1.379(6)$ | $\mathrm{C}(8)-\mathrm{C}(9)$ | $1.450(7)$ |
| $\mathrm{N}(3)-\mathrm{C}(15)$ | $1.388(6)$ | $\mathrm{C}(8)-\mathrm{C}(4)$ | $1.562(7)$ |
| $\mathrm{N}(4)-\mathrm{C}(25)$ | $1.372(6)$ | $\mathrm{C}(19)-\mathrm{C}(21)$ | $1.521(7)$ |
| $\mathrm{N}(4)-\mathrm{C}(22)$ | $1.377(6)$ | $\mathrm{C}(19)-\mathrm{C}(20)$ | $1.551(7)$ |
| $\mathrm{N}(2)-\mathrm{C}(11)$ | $1.300(6)$ | $\mathrm{C}(4)-\mathrm{C}(3)$ | $1.460(7)$ |
| $\mathrm{N}(2)-\mathrm{C}(8)$ | $1.443(6)$ | $\mathrm{C}(3)-\mathrm{C}(2)$ | $1.328(8)$ |
| $\mathrm{N}(5)-\mathrm{C}(29)$ | $1.122(7)$ | $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.458(7)$ |
| $\mathrm{C}(18)-\mathrm{C}(17)$ | $1.391(7)$ | $\mathrm{C}(1)-\mathrm{C}(26)$ | $1.513(7)$ |
| $\mathrm{C}(18)-\mathrm{C}(19)$ | $1.516(7)$ | $\mathrm{C}(29)-\mathrm{C}(30)$ | $1.449(8)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | $1.381(7)$ | $\mathrm{C}(26)-\mathrm{C}(28)$ | $1.541(7)$ |
| $\mathrm{C}(15)-\mathrm{C}(12)$ | $1.515(7)$ | $\mathrm{C}(26)-\mathrm{C}(27)$ | $1.543(7)$ |
| $\mathrm{C}(25)-\mathrm{C}(24)$ | $1.388(7)$ | $\mathrm{C}(9)-\mathrm{C}(10)$ | $1.340(8)$ |
| $\mathrm{C}(25)-\mathrm{C}(26)$ | $1.528(7)$ | $\mathrm{C}(16)-\mathrm{C}(17)$ | $1.406(8)$ |
| $\mathrm{C}(11)-\mathrm{C}(10)$ | $1.474(7)$ | $\mathrm{C}(23)-\mathrm{C}(24)$ | $1.400(7)$ |
| $\mathrm{C}(11)-\mathrm{C}(12)$ | $1.512(7)$ | $\mathrm{Cl}(2)-\mathrm{C}(31)$ | $1.678(11)$ |
| $\mathrm{C}(22)-\mathrm{C}(23)$ | $1.390(7)$ | $\mathrm{C}(31)-\mathrm{Cl}(1)$ | $1.826(11)$ |

Table S4. Bond angles (in deg) for $\left[\mathrm{L}^{\Delta} \mathrm{Mg}\left(\mathrm{CH}_{3} \mathrm{CN}\right)\right] \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

| Bond Angle | Angle | Bond Angle | Angle |
| :---: | :---: | :---: | :---: |
| $\mathrm{N}(3)-\mathrm{Mg}(1)-\mathrm{N}(4)$ | 93.25(16) | $\mathrm{C}(24)-\mathrm{C}(25)-\mathrm{C}(26)$ | 128.9(5) |
| $\mathrm{N}(3)-\mathrm{Mg}(1)-\mathrm{N}(5)$ | 106.58(17) | $\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{C}(10)$ | 111.2(4) |
| $\mathrm{N}(4)-\mathrm{Mg}(1)-\mathrm{N}(5)$ | 108.27(17) | $\mathrm{N}(2)-\mathrm{C}(11)-\mathrm{C}(12)$ | 120.6(4) |
| $\mathrm{N}(3)-\mathrm{Mg}(1)-\mathrm{N}(1)$ | 148.64(17) | $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(12)$ | 128.2(4) |
| $\mathrm{N}(4)-\mathrm{Mg}(1)-\mathrm{N}(1)$ | 87.89(16) | $\mathrm{N}(4)-\mathrm{C}(22)-\mathrm{C}(23)$ | 109.7(4) |
| $\mathrm{N}(5)-\mathrm{Mg}(1)-\mathrm{N}(1)$ | 102.75(17) | $\mathrm{N}(4)-\mathrm{C}(22)-\mathrm{C}(19)$ | 121.3(4) |
| $\mathrm{N}(3)-\mathrm{Mg}(1)-\mathrm{N}(2)$ | 87.13(16) | $\mathrm{C}(23)-\mathrm{C}(22)-\mathrm{C}(19)$ | 128.6(4) |
| $\mathrm{N}(4)-\mathrm{Mg}(1)-\mathrm{N}(2)$ | 147.59(17) | $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{C}(7)$ | 114.1(4) |
| $\mathrm{N}(5)-\mathrm{Mg}(1)-\mathrm{N}(2)$ | 102.61(17) | $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{C}(8)$ | 119.5(4) |
| $\mathrm{N}(1)-\mathrm{Mg}(1)-\mathrm{N}(2)$ | 75.77(15) | $\mathrm{C}(7)-\mathrm{C}(5)-\mathrm{C}(8)$ | 115.6(4) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(4)$ | 106.4(4) | $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{C}(4)$ | 120.3(4) |
| $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{Mg}(1)$ | 123.5(3) | $\mathrm{C}(7)-\mathrm{C}(5)-\mathrm{C}(4)$ | 116.0(4) |
| $\mathrm{C}(4)-\mathrm{N}(1)-\mathrm{Mg}(1)$ | 117.7(3) | $\mathrm{C}(8)-\mathrm{C}(5)-\mathrm{C}(4)$ | 61.4(3) |
| $\mathrm{C}(18)-\mathrm{N}(3)-\mathrm{C}(15)$ | 106.0(4) | $\mathrm{C}(11)-\mathrm{C}(12)-\mathrm{C}(15)$ | 107.7(4) |
| $\mathrm{C}(18)-\mathrm{N}(3)-\mathrm{Mg}(1)$ | 123.9(3) | $\mathrm{C}(11)-\mathrm{C}(12)-\mathrm{C}(14)$ | 110.8(4) |
| $\mathrm{C}(15)-\mathrm{N}(3)-\mathrm{Mg}(1)$ | 127.9(3) | $\mathrm{C}(15)-\mathrm{C}(12)-\mathrm{C}(14)$ | 110.6(4) |
| $\mathrm{C}(25)-\mathrm{N}(4)-\mathrm{C}(22)$ | 106.2(4) | $\mathrm{C}(11)-\mathrm{C}(12)-\mathrm{C}(13)$ | 108.3(4) |
| $\mathrm{C}(25)-\mathrm{N}(4)-\mathrm{Mg}(1)$ | 126.6(3) | $\mathrm{C}(15)-\mathrm{C}(12)-\mathrm{C}(13)$ | 111.9(4) |
| $\mathrm{C}(22)-\mathrm{N}(4)-\mathrm{Mg}(1)$ | 122.9(3) | $\mathrm{C}(14)-\mathrm{C}(12)-\mathrm{C}(13)$ | 107.6(4) |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{C}(8)$ | 106.4(4) | $\mathrm{N}(2)-\mathrm{C}(8)-\mathrm{C}(9)$ | 108.0(4) |
| $\mathrm{C}(11)-\mathrm{N}(2)-\mathrm{Mg}(1)$ | 122.5(3) | $\mathrm{N}(2)-\mathrm{C}(8)-\mathrm{C}(5)$ | 116.3(4) |
| $\mathrm{C}(8)-\mathrm{N}(2)-\mathrm{Mg}(1)$ | 117.5(3) | $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{C}(5)$ | 123.6(4) |
| $\mathrm{C}(29)-\mathrm{N}(5)-\mathrm{Mg}(1)$ | 174.4(4) | $\mathrm{N}(2)-\mathrm{C}(8)-\mathrm{C}(4)$ | 113.0(4) |
| $\mathrm{N}(3)-\mathrm{C}(18)-\mathrm{C}(17)$ | 110.0(4) | $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{C}(4)$ | 129.7(4) |
| $\mathrm{N}(3)-\mathrm{C}(18)-\mathrm{C}(19)$ | 121.8(4) | $\mathrm{C}(5)-\mathrm{C}(8)-\mathrm{C}(4)$ | 59.3(3) |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | 127.9(5) | $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(21)$ | 110.1(4) |
| $\mathrm{C}(16)-\mathrm{C}(15)-\mathrm{N}(3)$ | 110.4(4) | $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(22)$ | 113.4(4) |
| $\mathrm{C}(16)-\mathrm{C}(15)-\mathrm{C}(12)$ | 128.8(5) | $\mathrm{C}(21)-\mathrm{C}(19)-\mathrm{C}(22)$ | 108.9(4) |
| $\mathrm{N}(3)-\mathrm{C}(15)-\mathrm{C}(12)$ | 120.8(4) | $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | 108.3(4) |
| $\mathrm{N}(4)-\mathrm{C}(25)-\mathrm{C}(24)$ | 110.6(4) | $\mathrm{C}(21)-\mathrm{C}(19)-\mathrm{C}(20)$ | 108.1(4) |
| $\mathrm{N}(4)-\mathrm{C}(25)-\mathrm{C}(26)$ | 120.4(4) | $\mathrm{C}(22)-\mathrm{C}(19)-\mathrm{C}(20)$ | 107.8(4) |

Table S4 cont'd

| Bond Angle | Angle | Bond Angle | Angle |
| ---: | ---: | ---: | ---: |
| $\mathrm{N}(1)-\mathrm{C}(4)-\mathrm{C}(3)$ | $107.5(4)$ | $\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{C}(28)$ | $110.2(4)$ |
| $\mathrm{N}(1)-\mathrm{C}(4)-\mathrm{C}(5)$ | $118.3(4)$ | $\mathrm{C}(1)-\mathrm{C}(26)-\mathrm{C}(27)$ | $109.7(4)$ |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | $122.2(4)$ | $\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{C}(27)$ | $109.7(4)$ |
| $\mathrm{N}(1)-\mathrm{C}(4)-\mathrm{C}(8)$ | $113.2(4)$ | $\mathrm{C}(28)-\mathrm{C}(26)-\mathrm{C}(27)$ | $108.6(4)$ |
| $\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(8)$ | $129.9(4)$ | $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(8)$ | $106.9(4)$ |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(8)$ | $59.3(3)$ | $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)$ | $106.8(4)$ |
| $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | $106.6(5)$ | $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | $107.1(5)$ |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | $111.2(4)$ | $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{C}(1)$ | $108.0(4)$ |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(26)$ | $120.9(4)$ | $\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(24)$ | $107.2(4)$ |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(26)$ | $127.8(4)$ | $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{C}(16)$ | $106.9(4)$ |
| $\mathrm{N}(5)-\mathrm{C}(29)-\mathrm{C}(30)$ | $179.5(7)$ | $\mathrm{C}(25)-\mathrm{C}(24)-\mathrm{C}(23)$ | $106.2(4)$ |
| $\mathrm{C}(1)-\mathrm{C}(26)-\mathrm{C}(25)$ | $107.8(4)$ | $\mathrm{Cl}(2)-\mathrm{C}(31)-\mathrm{Cl}(1)$ | $109.4(6)$ |
| $\mathrm{C}(1)-\mathrm{C}(26)-\mathrm{C}(28)$ | $110.7(4)$ |  |  |

Table S5. Anisotropic thermal displacement parameters ( $\AA^{2} \times 10^{3}$ ) for $\left[L^{\Delta} \mathrm{Mg}\left(\mathrm{CH}_{3} \mathrm{CN}\right)\right] \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

| Atom | $\mathrm{U}_{11}$ | $\mathrm{U}_{22}$ | $\mathrm{U}_{33}$ | $\mathrm{U}_{23}$ | $\mathrm{U}_{13}$ | $\mathrm{U}_{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Mg}(1)$ | 23(1) | 23(1) | 21(1) | 1(1) | -3(1) | -8(1) |
| $\mathrm{N}(1)$ | 25(2) | 23(2) | 27(2) | 0 (2) | -3(2) | -9(2) |
| N(3) | 26(2) | 21(2) | 25(2) | 2(2) | 0(2) | -8(2) |
| N(4) | 24(2) | 25(2) | 25(2) | -3(2) | 1(2) | -7(2) |
| $\mathrm{N}(2)$ | 25(2) | 25(2) | 25(2) | 2(2) | -3(2) | -11(2) |
| N(5) | 36(3) | 37(3) | 27(2) | -2(2) | -5(2) | -9(2) |
| C(18) | 28(3) | 26(3) | 24(3) | 5(2) | -2(2) | -9(2) |
| C(15) | 27(3) | 24(3) | 23(3) | 1(2) | -1(2) | -5(2) |
| C(25) | 26(3) | 30(3) | 23(3) | -3(2) | 0 (2) | -6(2) |
| C(11) | 20(2) | 28(3) | 26(3) | -2(2) | 0 (2) | -10(2) |
| C(22) | 26(3) | 29(3) | 20(2) | -2(2) | 4(2) | -13(2) |
| C(5) | 28(3) | 30(3) | 37(3) | 2(2) | -3(2) | -13(2) |
| C(12) | 27(3) | 27(3) | 27(3) | -3(2) | 1(2) | -4(2) |
| C(8) | 28(3) | 29(3) | 24(3) | 2(2) | $0(2)$ | -14(2) |
| C(19) | 30(3) | 29(3) | 28(3) | 2(2) | 3(2) | -13(2) |
| C(4) | 28(3) | 26(3) | 29(3) | 6(2) | -5(2) | -13(2) |
| C(3) | 33(3) | 35(3) | 33(3) | 11(2) | -9(2) | -18(2) |
| C(1) | 27(3) | 21(2) | 32(3) | 0 (2) | -6(2) | -11(2) |
| C(29) | 37(3) | 41(3) | 26(3) | -5(2) | -5(3) | -11(3) |
| C(26) | 30(3) | 25(3) | 36(3) | -1(2) | -5(2) | -7(2) |
| C(9) | 34(3) | 40(3) | 23(3) | 3(2) | -1(2) | -16(2) |
| C(16) | 37(3) | 21(3) | 30(3) | -2(2) | -2(2) | -5(2) |
| C(10) | 35(3) | 42(3) | 25(3) | -7(2) | 2(2) | -17(2) |
| C(27) | 40(3) | 31(3) | 39(3) | -8(2) | -7(2) | -12(2) |
| C(2) | 27(3) | 27(3) | 45(3) | 11(2) | -14(2) | -8(2) |
| C(20) | 45(3) | 38(3) | 28(3) | 4(2) | 1(2) | -10(3) |
| C(23) | 28(3) | 37(3) | 23(3) | -3(2) | 1(2) | -17(2) |
| C(13) | 27(3) | 35(3) | 38(3) | 1(2) | -5(2) | -3(2) |
| C(14) | 31(3) | 29(3) | 43(3) | -8(2) | 3(2) | -6(2) |
| C(17) | 39(3) | 21(3) | 34(3) | 3(2) | -2(2) | -16(2) |
| C(24) | 23(3) | 35(3) | 26(3) | -6(2) | -3(2) | -8(2) |
| C(28) | 33(3) | 29(3) | 52(4) | -8(3) | -3(3) | -4(2) |
| C(21) | 35(3) | 34(3) | 48(3) | 2(3) | 9(3) | -17(2) |
| C(6) | 32(3) | 36(3) | 48(3) | -4(3) | -7(2) | -14(2) |
| C(7) | 37(3) | 37(3) | 48(3) | 3(3) | 3(3) | -20(3) |
| C(30) | 70(5) | 109(7) | 48(4) | -10(4) | -30(4) | -30(5) |
| $\mathrm{Cl}(2)$ | 309(7) | 195(5) | 110(3) | 4(3) | 9(4) | -80(5) |
| C(31) | 77(6) | 115(7) | 50(5) | 24(5) | -5(4) | -25(5) |
| $\mathrm{Cl}(1)$ | 165(4) | 153(3) | 134(3) | -12(2) | 15(3) | -10(3) |

The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U_{11}+\ldots+2 h k a * b * U_{12}\right]$.

Table S6. Hydrogen coordinates $\left(\times 10^{4}\right)$ and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\left[\mathrm{L}^{\mathrm{A}} \mathrm{Mg}\left(\mathrm{CH}_{3} \mathrm{CN}\right)\right] \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

| Atom | x | y | z | $\mathrm{U}_{\text {eq }}$ |
| :---: | :---: | :---: | :---: | :---: |
| H(3) | 333 | 7956 | 4569 | 40 |
| H(9) | 2417 | 5341 | 4035 | 38 |
| H(16) | 1805 | -196 | 6403 | 36 |
| H(10) | 3247 | 2913 | 4390 | 39 |
| H(27A) | -214 | 6695 | 8544 | 54 |
| H(27B) | -1615 | 7535 | 8970 | 54 |
| H(27C) | -642 | 8275 | 8341 | 54 |
| H(2) | -1625 | 8843 | 5601 | 41 |
| H(20A) | -357 | 1496 | 9458 | 57 |
| H(20B) | -1478 | 2818 | 9674 | 57 |
| H(20C) | -54 | 2902 | 9198 | 57 |
| H(23) | -4009 | 4273 | 7886 | 34 |
| H(13A) | 4815 | 2188 | 6973 | 52 |
| H(13B) | 4357 | 988 | 7572 | 52 |
| H(13C) | 3526 | 2482 | 7684 | 52 |
| H(14A) | 3396 | 754 | 5325 | 52 |
| H(14B) | 4175 | -64 | 6228 | 52 |
| $\mathrm{H}(14 \mathrm{C})$ | 4765 | 1007 | 5569 | 52 |
| H(17) | -459 | 181 | 7290 | 37 |
| $\mathrm{H}(24)$ | -4208 | 6725 | 7550 | 33 |
| H(28A) | -2551 | 9441 | 7284 | 58 |
| H(28B) | -3479 | 8680 | 7944 | 58 |
| H(28C) | -3331 | 8592 | 6834 | 58 |
| H(21A) | -2687 | 1854 | 7700 | 58 |
| H(21B) | -3096 | 2223 | 8749 | 58 |
| H(21C) | -1961 | 891 | 8575 | 58 |
| H(6A) | 3289 | 7339 | 6803 | 56 |
| H(6B) | 4314 | 5981 | 6548 | 56 |
| H(6C) | 2962 | 5964 | 7163 | 56 |
| H(7A) | 2988 | 8272 | 5038 | 59 |
| H(7B) | 2684 | 7334 | 4354 | 59 |
| H(7C) | 4118 | 6968 | 4799 | 59 |
| H(30A) | 3899 | 3459 | 10162 | 109 |
| H(30B) | 2887 | 4786 | 10481 | 109 |
| H(30C) | 4083 | 4869 | 9719 | 109 |
| H(31A) | 2202 | 10417 | 8501 | 101 |
| H(31B) | 1726 | 9703 | 9475 | 101 |

Table S7. Energies of the frontier and near-frontier orbitals of [ $\mathrm{L}^{\Delta} \mathrm{Mg}\left(\mathrm{CH}_{3} \mathrm{CN}\right)$ ] according to the SP DFT (GGA Becke88x/PW91, TZ2P) calculation.

| MO No. | Occup. | Energy (eV) | MO No. | Occup. | Energy (eV) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 86 | 2.000 | -6.540 | 96 | 0.000 | -2.379 |
| 87 | 2.000 | -6.431 | 97 | 0.000 | -1.771 |
| 88 | 2.000 | -6.267 | 98 | 0.000 | -1.198 |
| 89 | 2.000 | -6.067 | 99 | 0.000 | -1.198 |
| 90 | 2.000 | -6.043 | 100 | 0.000 | -0.462 |
| 91 | 2.000 | -5.401 | 101 | 0.000 | 0.333 |
| 92 | 2.000 | -4.088 | 102 | 0.000 | 0.386 |
| 93 | 2.000 | -3.932 | 103 | 0.000 | 0.708 |
| 94 | 2.000 | -3.234 | 104 | 0.000 | 0.849 |
| 95 | 2.000 | -3.103 | 105 | 0.000 | 0.939 |

Table S8. Atomic charges of $\left[\mathrm{L}^{\Delta} \mathrm{Mg}\left(\mathrm{CH}_{3} \mathrm{CN}\right)\right]$ according to the Mulliken population analysis, with atom numbering scheme used for calculation provided below.

| Atom | Charge | Atom | Charge | Atom | Charge | Atom | Charge |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 Mg | 1.2071 | 19 C | 0.2394 | 37 H | 0.3914 | 55 H | 0.3847 |
| 2 N | -0.5044 | 20 C | -0.2014 | 38 H | 0.3897 | 56 H | 0.3915 |
| 3 N | -0.6007 | 21 C | 0.4031 | 39 H | 0.3902 | 57 H | 0.3439 |
| 4 N | -0.6991 | 22 C | 0.2781 | 40 H | 0.3634 | 58 H | 0.3217 |
| 5 N | -0.501 | 23 C | 0.3305 | 41 H | 0.2342 | 59 H | 0.3257 |
| 6 N | -0.3113 | 24 C | 0.9641 | 42 H | 0.3438 | 60 H | 0.3259 |
| 7 C | 0.2916 | 25 C | 0.3394 | 43 H | 0.367 | 61 H | 0.3397 |
| 8 C | 0.2639 | 26 C | 0.9508 | 44 H | 0.3637 | 62 H | 0.3437 |
| 9 C | 0.3279 | 27 C | 0.2969 | 45 H | 0.3447 | 63 H | 0.3345 |
| 10 C | 0.3384 | 28 C | 0.9643 | 46 H | 0.341 | 64 H | 0.3297 |
| 11 C | 0.311 | 29 C | 0.9169 | 47 H | 0.2822 | 65 H | 0.1909 |
| 12 C | 0.0391 | 30 C | 0.2743 | 48 H | 0.3821 | 66 H | 0.2802 |
| 13 C | -0.1985 | 31 C | 0.2603 | 49 H | 0.3621 | 67 H | 0.3429 |
| 14 C | 0.1897 | 32 C | 0.9153 | 50 H | 0.3512 | 68 H | 0.2941 |
| 15 C | -0.1965 | 33 C | 0.9311 | 51 H | 0.2423 | 69 H | 0.1897 |
| 16 C | 0.186 | 34 C | 0.9308 | 52 H | 0.3293 | 70 H | 0.1921 |
| 17 C | 0.4082 | 35 C | 0.8926 | 53 H | 0.3196 |  |  |
| 18 C | 0.3396 | 36 C | 0.6932 | 54 H | 0.3449 |  |  |




[^0]:    ${ }^{\mathrm{a}} \mathrm{U}_{\mathrm{eq}}$ is defined as one third of the trace of the orthogonalized $\mathrm{U}_{\mathrm{ij}}$ tensor.

