Synthesis and Characterisation of Luminescent 
[Cr$^{III}_2$L($\mu$-carboxylato)]$^{3+}$ Complexes with High-Spin $S = 3$ 
Ground States ($L = N_6S_2$ donor ligand)

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Supporting Information

Contents

1. ESI MS Data for 1 and 2.
2. IR spectra for 1 and 2.
3. Molecular structure of the [Cr$^{III}_{2}$L(μ-O$_2$CPh)]$^{3+}$ cation in crystals of 2·3MeCN.
4. Magnetic susceptibility data for 1 and 2.
5. Diffuse-reflectance spectroscopy for 1 and 2.
6. Photoluminescence excitation and emission spectra for 1 and 2 at 77 K.
7. Time resolved photoluminescence decay measurements for 1 and 2 at 77 K.
8. Photoluminescence excitation and emission spectra for 1 and 2 at 298 K.
9. Time resolved photoluminescence decay measurements for 1 and 2 at 298 K.
10. Photoluminescence spectra of 1 and 2 at 298 K.
11. PLIM (phosphorescence lifetime microscopy) for complex 2.
12. Cartesian coordinates / Å of geometry optimized [Cr$^{III}_{2}$L(μ-O$_2$CMe)]$^{3+}$ (1, gas phase).
13. Cartesian coordinates / Å of geometry optimized [Cr$^{III}_{2}$L(μ-O$_2$CPh)]$^{3+}$ (2, gas phase).
14. Cartesian coordinates / Å of [Cr$^{III}_{2}$L]$^{4+}$ (1′, gas phase).
15. Cartesian coordinates / Å of [Cr$^{III}_{2}$L]$^{4+}$ (2′, gas phase).
1. ESI MS Data for 1 and 2

Figure S1. ESI(−) mass spectrum of [Cr$_{2}$(μ-O$_{2}$CMe)][ClO$_{4}$]$_{3}$ (1) in MeCN ($c \sim 10^{-3}$ M).

Figure S2. ESI(−) mass spectrum of [Cr$_{2}$(μ-O$_{2}$CPh)][ClO$_{4}$]$_{3}$ (2) in MeCN ($c \sim 10^{-3}$ M).
2. IR spectra for 1 and 2.

**Figure S3.** FT-IR spectrum of $\text{[Cr}^{\text{III}}_2\text{L(μ-O}_2\text{CMe)}\text{]}\text{(ClO}_4\text{)}_3$ (1, KBr pellet).

**Figure S4.** FT-IR spectrum of $\text{[Cr}^{\text{III}}_2\text{L(μ-O}_2\text{CPh)}\text{]}\text{(ClO}_4\text{)}_3$ (2, KBr pellet).
**Figure S5.** Molecular structure of the $\text{[Cr}^{III}_2\text{L(μ-O}_2\text{CPh)}]^{3+}$ cation (one of two crystallographically independent cations) in crystals of 2:$x$MeCN ($x \sim 4.5$). Thermal ellipsoids are drawn at the 50% probability level. Only one orientation of a disordered tert-butyl group is shown. Hydrogen atoms are omitted for reasons of clarity.
4a. Magnetic susceptibility data for 1\( \text{H}_2\text{O} \) and 2\( \text{4.5MeCN} \).

**Table S1.** Experimental and calculated susceptibility data for 1\( \text{H}_2\text{O} \) and 2\( \text{4.5MeCN} \). The susceptibility data were fitted with the program PHL."
Complex 12H2O
============================================
Finished Simplex with 363 iterations
                  24.198286508554695 +/- 0.14373563133094
EX 1 2 4
               1.9848197219152126 +/- 0.00057248861705
GF 1 4 0
GF 2 4 0
                -0.0053281506032641 +/- 0.00026154325851
ZJ 0 0 0
--------- Parameter Correlations ---------
 If magnitude of correlation is > 0.8,
then a strong correlation is present.
1 2 -0.6
1 3  0.3
2 3 -0.5

Residual: 0.58284969746703105E-003
Residual reduced by: 0.08226134107584269
or: 99.296450732361052%
============================================
Complex 24.5MeCN
============================================
Finished Simplex with 368 iterations
                  34.781805912573134 +/- 0.38320658978043
EX 1 2 4
               1.9791253199624190 +/- 0.00041132430980
GF 1 4 0
GF 2 4 0
                -0.0057419642080043 +/- 0.00046403439556
ZJ 0 0 0
--------- Parameter Correlations ---------
 If magnitude of correlation is > 0.8,
then a strong correlation is present.
1 2 -0.3
1 3  0.0
2 3 -0.2

Residual: 0.00126862152004810
Residual reduced by: 0.25585760976702432
or: 99.506615286313689%
**Figure S6.** Plot of the magnetization (M) versus field (B) for compound \textbf{1·2H}_2\textbf{O} at \(T = 2\text{K}\). The solid line was fitted with the program PHI (option opmode fit sm, parameters: J, g, zJ). Resultant fit parameters are given above. The plot was generated with the program PHI.

**Figure S7.** Plot of the magnetization (M) versus field (B) for compound \textbf{2·4.5MeCN} at \(T = 2\text{K}\). The solid line was fitted with the program PHI (option opmode fit sm, parameters: J, g, zJ). Resultant fit parameters are given above. The plot was generated with the program PHI.
Figure S8. Pairs of “magnetic orbitals” for 1 derived from the corresponding orbital transformation of the broken-symmetry DFT determinant. The $S$ values correspond to the values of overlap integrals for the corresponding orbital pairs.
Figure S9. Pairs of “magnetic orbitals” for 2 derived from the corresponding orbital transformation of the broken-symmetry DFT determinant. The $S$ values correspond to the overlap integrals for the corresponding orbital pairs.
4b. Results of Broken-symmetry DFT calculations for complexes 1 and 2.

Table S2. Calculated Mulliken spin density and $J$ values of complexes 1 and 2 at the B3LYP/def2-TZVPP level of theory.

| Compd | state | Cr1 | Cr2 | S1  | S2  | O1  | O2  | N1-N6 | Total spin | $J$ / cm$^{-1}$ |
|-------|-------|-----|-----|-----|-----|-----|-----|-------|------------|----------------|
| 1     | HS    | 3.295 | 3.294 | -0.143 | -0.152 | -0.0149 | -0.0144 | -0.061 to -0.073 | 6           | +31.07        |
|       | BS    | 3.276 | -3.276 | 0.0005 | 0.0012 | -0.0359 | 0.03469 | -0.066 to -0.073 (3x) | 0           |               |
| 2     | HS    | 3.285 | 3.291 | -0.0143 | -0.0153 | -0.0136 | -0.0141 | -0.060 to -0.073 | 0           |               |
|       | BS    | 3.263 | -3.268 | 0.0004 | 0.0003 | -0.032 | 0.033 | -0.065 to -0.073 (3x) | 0           |               |

*a) The $J$ values are based on the energy difference between the high-spin and broken-symmetry solutions as calculated by the Yamaguchi formula, i.e. $J = -(E_{HS} - E_{BS}) / (\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS})$.

4c. Results of Broken-symmetry DFT calculations for complexes 1’ and 2’.

In order to evaluate the coupling through the thiophenolato and carboxylato bridges in the present complexes, we utilized a breakdown approach, in which the carboxylate ligands were virtually removed from the optimized structures of 1 and 2 to obtain the hypothetical $[\text{Cr}_2(L)]^{4+}$ dications 1’ and 2’, respectively. These cations were also subjected to broken symmetry DFT density functional theory calculations. This method has previously shown to be a powerful tool to unravel the contribution of the various bridging co-ligands for dinuclear nickel complex of the type $[\text{Ni}_2L(\mu-L')]^+$, where $L = \text{F}^-$, $\text{Cl}^-$, $\text{Br}^-$, $\text{N}_3^-$, and $\text{OH}^-$. The coupling constants ($J_{SR}$) calculated for the $[\text{Cr}_2(L)]^{4+}$ cations 1’ ($J = +39.85$ cm$^{-1}$) and 2’ ($J = +41.13$ cm$^{-1}$) were found to be slightly larger than for the carboxylato-bridged species, indicative of an orbital counter-complementary effect. A similar effect was observed for the series of carboxylato-bridged chromium(III) complexes reported by Rajaraman and Brechin.

Table S3. Calculated Mulliken spin density and $J$ values of complexes 1’ and 2’ at the B3LYP/def2-TZVPP level of theory.

| Compd | state | Cr1 | Cr2 | S1  | S2  | N1-N6 | Total spin | $J$ / cm$^{-1}$ |
|-------|-------|-----|-----|-----|-----|-------|------------|----------------|
| 1’    | HS    | 3.450 | 3.451 | -0.316 | -0.281 | -0.076 to -0.142 | 6           | +39.85        |
|       | BS    | 3.212 | -3.213 | -0.0009 | 0.00107 | -0.031 to -0.078 (3x) | 0           |               |
| 2’    | HS    | 3.458 | 3.464 | -0.1601 | -0.1669 | -0.076 to -0.155 | 6           | +41.13        |
|       | BS    | 3.400 | -3.400 | -0.0010 | 0.0004 | -0.080 to -0.144 (3x) | 0           |               |

*a) The $J$ values are based on the energy difference between the high-spin and broken-symmetry solutions as calculated by the Yamaguchi formula, i.e. $J = -(E_{HS} - E_{BS}) / (\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS})$. 
5. Diffuse-reflectance spectroscopy for 1 and 2.

**Figure S10.** Kubelka-Munk converted diffuse reflectance UV-vis spectrum for 1 (solid black curve) and 2 (blue dashed curve) (~ 5 wt% finely dispersed in BaSO₄ powder) at 298 K.

6. Photoluminescence excitation and emission spectra for 2 at 77 K.

**Figure S11.** Photoluminescence excitation ($\lambda_{\text{obs}}$ = 750 nm, dotted curve) and emission spectra ($\lambda_{\text{exc}}$ = 405 nm, solid line) of complex 2 at 77 K in CH₂Cl₂/MeOH (1:1) glassy matrix.
7. Time resolved photoluminescence decay measurements for 1 and 2 at 77 K.

Figure S12. Left: Time-resolved photoluminescence decay of 1 in a frozen glassy matrix of CH₂Cl₂/MeOH 1:1 at 77 K, including the residuals (λ_{exc} = 402.5 nm, λ_{em} = 750 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

Figure S13. Left: Time-resolved photoluminescence decay of 2 in a frozen glassy matrix of CH₂Cl₂/MeOH 1:1 at 77 K, including the residuals (λ_{exc} = 402.5 nm, λ_{em} = 750 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

Table S4. Photophysical data for 1 and 2 in a frozen CH₂Cl₂/MeOH 1:1 glassy matrix at 77 K.

| R    | τ (μs) | \( \lambda_{\text{exc}} \) (nm) | \( \lambda_{\text{em}} \) (nm) | \( \Phi_L \) (%) | \( k_r / 10^3 \) (s⁻¹) | \( k_{nr} / 10^3 \) (s⁻¹) |
|------|--------|-------------------------------|-------------------------------|----------------|----------------------|----------------------|
| CH₃  | 113.0±0.8 | 405 | 750 | 45±2 | 3.98 ± 0.03 | 4.87 ± 0.03 |
| C₆H₅ | 114.6±0.9 | 405 | 750 | 44±2 | 3.84 ± 0.03 | 5.90 ± 0.04 |
8. Photoluminescence excitation and emission spectra for 1 and 2 at 298 K.

![Photoluminescence spectra](image1.png)

**Figure S14.** Photoluminescence emission spectra for [Cr₂L(μ-O₂CR)](ClO₄)₃ (R = Me, red curve 1; R = Ph blue curve 2) at 298 K in deaerated MeOH solution.

9. Time resolved photoluminescence decay measurements for 1 and 2 at 298 K.

![Time-resolved decay](image2.png)

**Figure S15.** Left: Time-resolved photoluminescence decay of 1 in deaerated MeOH solution at 298 K, including the residuals (λ_{exc} = 372.5 nm, λ_{em} = 710 nm). Right: Fitting parameters including pre-exponential factors and confidence limits.
Figure S16. Left: Time-resolved photoluminescence decay of 2 in deaerated MeOH solution at 298 K, including the residuals ($\lambda_{\text{exc}} = 372.5$ nm, $\lambda_{\text{em}} = 710$ nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

Table S5. Photophysical data for 1 and 2 in degassed MeOH at 298 K.

| Compound | $\tau$ (ns) | $\Phi_L$ (%) | $k_r / 10^5$ (s$^{-1}$) | $k_{nr} / 10^7$ (s$^{-1}$) |
|----------|-------------|--------------|-------------------------|---------------------------|
| 1        | 75.3 ± 0.3  | < 2          | < 2.6                   | 1.33 > $k_{nr}$ > 1.30   |
| 2        | 94.8 ± 0.4  | < 2          | < 2.1                   | 1.05 > $k_{nr}$ > 1.03   |

10. Photoluminescence spectra of 1 and 2 at 298 K.

Figure S17. Emission spectra ($\lambda_{\text{exc}} = 355$ nm) of powdered solid samples of complexes 1 and 2 at 298 K obtained with an iHR320, synapse CCD, HORIBA JobinY spectrometer. The splitting of the signal ($\lambda_{\text{max}} = 706$ nm, 725 nm) may be due to emission from the $^2T_1^4A_2$ and $^2E^4A_2$ states.
11. PLIM (phosphorescence lifetime microscopy) for complex 2.

To measure the luminescence lifetime of solid 2 at ambient temperature, Phosphorescence lifetime microscopy (PLIM) was used. PLIM is based on the combination of local imaging using a microscope and luminescence lifetime detection based of time-correlated single photon counting (TCSPC). TCSPC detects the time difference between the excitation pulse and the photon emitted by the sample during the transition from the excited state to the energetically lower state. A TCSPC histogram is generated from the multiple repetitions of the time measurement and accumulation of the detected time differences, since the emission of photons follows a Poisson distribution, there is an exponential drop for the histogram. This histogram can be adapted to the exponential function (eq. 1).

\[ I(t) = I_0 \times e^{-\frac{t}{\tau}} \]  

(1)

Since the initial luminescence intensity of the sample \( I_0 \), the time \( t \) and the luminescence intensity \( (I(t)) \) after the time \( t \) are known, the luminescence lifetime \( \tau \) can be extracted therefrom. At the same time, the luminescence lifetime is inversely proportional to the sum of all deactivated states \( k_i \) (eq. 2). \( k_i \) includes e.g. the lattice relaxation, the electron transfer between different states etc. According to the Becker & Hickl application note, burst mode (burst of multiple laser pulses) was applied to TCSPC to increase the excitation efficiency of phosphorescence and to improve the detection of the phosphorescence lifetime.

\[ \frac{1}{\tau} = \sum k_i \]  

(2)

The luminescence lifetime is measured as a function of the position of the sample, so several \( \tau \) values are assigned to each xy position in order to build up the luminescence lifetime image. The service life is coded in a color scheme.
Figure S18. PLIM investigations of a powdered sample of complex 2 under ambient conditions: 
a) time decay profile (black) and the mono-exponential fit function (Becker & Hickl, red) of its 
luminescence under 405 nm excitation (diode laser, 60 ps pulse duration, 80 MHz repetition rate, 
60 µs burst duration, Becker & Hickl) with a 542 nm long pass filter, b) spatially resolved PLIM 
image for τ1 transient, c) phosphorescence lifetime distribution of complex 2 based on image b, 
the averaged phosphorescence lifetime was determined at 35 µs.

12. Cartesian coordinates / Å of geometry optimized [CrIII2L(μ-O2CMe)]3+ (1, gas phase).

Table S6. Cartesian coordinates / Å of geometry optimized [CrIII2L(μ-O2CMe)]3+ (1, gas 
phase, B3LYP/def2-TZVPP).

| Atom | x (Å) | y (Å) | z (Å) |
|------|-------|-------|-------|
| C    | 5.42035752591941 | 12.59651182236640 | 8.59415089835852 |
| C    | 5.87724780519012  | 13.17382092970474  | 9.78259974779086  |
| C    | 6.75848324949109  | 12.46211454747514  | 10.58805753792097 |
| H    | 7.06410351419183  | 12.91043872333443  | 11.52320610117925 |
| C    | 7.17631972312593  | 11.16177223872840  | 10.288744326287508 |
| C    | 6.67927942101886  | 10.60853197377671  | 9.11228925314978  |
| C    | 6.91551979919126  | 9.58488449749747   | 8.8631650810132   |
| C    | 5.81128952236335  | 11.29918944836357  | 8.26787939165447  |
| C    | 5.10376426510658  | 10.53375945994515  | 7.20205683659817  |
| H    | 4.03941912078201  | 10.63576313703607  | 7.36198369594896  |
| H    | 5.36624889797280  | 9.47638129461854    | 7.31752724647865  |
| C    | 6.7505376777580   | 10.3962417595743   | 5.45484098217942  |
| C    | 6.94349889551726  | 10.4665742043166    | 4.3897180426058  |
| H    | 7.47190502626959  | 11.00090401054879  | 5.93629910175451  |
| H    | 6.86033673778473  | 9.35150443628145    | 5.75132851209968  |
| C    | 4.36759842245456  | 10.9057563614247    | 4.9567142952322  |
| H    | 4.74508516234941  | 9.90809021679097    | 3.9833115823269  |
| C    | 4.21765041041058  | 9.11524121855014    | 5.4421329595794  |
| H    | 3.06253927083989  | 10.8528958247638    | 4.96059403836106  |
| C    | 2.66044537357938  | 10.96366932549854   | 5.96450626723742  |
| C    | 2.31676331966969  | 10.3103466802111    | 4.37632892736642  |
| C    | 1.99820247281566  | 12.999084982606826  | 4.66193548032011  |
| H    | 1.83491215950544  | 13.05206329464091   | 5.73421612479510  |
| H    | 2.09329604624383  | 13.99932044082325   | 4.2656103465569  |
| C    | 1.14355673657658  | 12.49446564001610   | 4.19873056710186  |
| C    | 3.4603898909813   | 12.13621644803172   | 2.91251460175183  |
| C    | 2.98190039095786  | 13.0087234898566    | 2.46411424908436  |
| C    | 2.94520151362393  | 11.25985237839145   | 2.51684268612872  |
| C    | 4.92690452752520  | 12.09167322979756   | 2.51840885265278  |
| C    | 5.00608558843668  | 12.18401476969508   | 1.4319943170328  |
| C    | 5.3903691190685   | 11.5209282897875    | 2.7807310919894  |
| C    | 7.1435707851022   | 12.9877622988741    | 2.9872887330303  |
13. Cartesian coordinates / Å of geometry optimized [CrII(μ-O2CPh)]+ (2, gas phase).

Table S7. Cartesian coordinates / Å of geometry optimized [CrII(μ-O2CPh)]+ (2, gas phase, B3LYP/def2-TZVPP).

| Atom | x        | y        | z        |
|------|----------|----------|----------|
| C    | 4.9738... | 9.7964... | 12.738... |
| C    | 3.7947... | 9.4226... | 13.375... |
| C    | 3.8565... | 8.6306... | 14.518... |
| H    | 9.2670... | 8.3344... | 14.981... |
| H    | 5.5607... | 1.8152... | 15.038... |
| H    | 6.2233... | 8.5243... | 14.351... |
| H    | 7.1782... | 8.1408... | 14.685... |
| H    | 6.1970... | 9.3198... | 13.210... |
| H    | 7.4299... | 9.4901... | 12.383... |
| H    | 7.2177... | 9.1499... | 11.373... |
| H    | 8.2215... | 8.8540... | 12.783... |
| H    | 8.3540... | 11.2901...| 13.647... |
| H    | 9.6037... | 10.5738...| 14.007... |
| H    | 4.7507... | 11.3167...| 14.285... |
| H    | 8.8062... | 12.2735...| 13.678... |
| H    | 9.2080... | 11.9963...| 11.439... |
| H    | 9.8522... | 9.9843... | 11.779... |
| H    | 9.7729... | 11.7146...| 11.572... |
| H    | 8.8345... | 10.5893...| 9.983... |
| H    | 8.4379... | 9.5656... | 8.503... |
| H    | 9.7224... | 10.6457...| 9.354... |
| H    | 6.9249... | 10.8149...| 8.4891... |
| H    | 6.1806... | 11.5105...| 8.1112... |
| H    | 6.4228... | 9.9748... | 8.9565... |
| H    | 7.5325... | 7.1049... | 7.6551... |
| H    | 6.4078... | 12.6762...| 8.8010... |
| H    | 7.6149... | 13.2157...| 8.2865... |
| H    | 9.1042... | 12.3195...| 8.0392... |
| H    | 9.1157... | 13.5779...| 7.9834... |
| H    | 9.9597... | 13.0768...| 10.2449...|
| H    | 9.5244... | 14.4471...| 9.2642... |
| H    | 8.9140... | 14.4574...| 12.0477...|
| H    | 9.4867... | 13.6369...| 12.4621...|
| H    | 8.2105... | 14.6222...| 12.7995...|
| H    | 6.9083... | 12.5757...| 11.7833...|
| H    | 7.4578... | 13.2317...| 10.3054...|
| H    | 7.7139... | 15.0007...| 9.2801... |
| H    | 8.1966... | 16.0341...| 10.2689...|
| H    | 6.2440... | 15.7167...| 11.0385...|
| H    | 5.0083... | 15.1167...| 10.7751...|
| H    | 3.9163... | 15.7725...| 11.1474...|
| H    | 2.9938... | 17.4195...| 12.1833...|
| H    | 5.1300... | 17.4686...| 12.3637...|
| H    | 6.2854... | 16.8712...| 11.9833...|
| H    | 7.2461... | 17.3532...| 10.5760...|
| H    | 2.5306... | 15.9497...| 9.5355... |
14. Cartesian coordinates / Å of \([\text{Cr}^{\text{III}}_2\text{L}]^{4+}\) (1′, gas phase).

**Table S8.** Cartesian coordinates / Å of \([\text{Cr}^{\text{III}}_2\text{L}]^{4+}\) (1′).

| atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | 5.4258| 12.5973| 8.59531|
| C    | 5.88027| 13.17455| 9.78393|
| C    | 6.76004| 12.46303| 10.59122|
| H    | 7.06444| 12.91168| 11.52674|
| C    | 7.17733| 11.16264| 10.29207|
| C    | 6.68226| 10.60921| 9.11489|
| H    | 6.91668| 9.58594| 8.86558|
| C    | 5.81506| 11.30002| 8.27086|
| C    | 5.10568| 10.5357| 7.2052|
| H    | 4.03562| 10.64115| 7.36712|
| H    | 4.42124| 9.12091| 5.44766|
| C    | 3.66047| 10.86202| 4.96791|
| C    | 2.65966| 10.97633| 5.97208|
| H    | 2.31145| 10.32295| 4.38481|
| C    | 2.00474| 13.00336| 4.66486|
| H    | 1.8425| 13.06958| 5.73762|
| H    | 2.10225| 14.00434| 4.25849|
| H    | 1.14849| 12.50712| 4.20491|
| C    | 3.46391| 12.13973| 2.91828|
| H    | 2.98775| 13.00465| 2.46756|
| C    | 2.94644| 11.26374| 2.52482|
| C    | 4.92989| 12.09088| 2.52436|
| H    | 5.00947| 12.18341| 1.43804|
| H    | 5.3987| 11.15003| 2.78636|
| C    | 7.14911| 12.97397| 2.99253|
| H    | 7.68326| 13.8403| 3.38015|
| H    | 7.48197| 12.09147| 3.52176|
| H    | 7.37126| 12.86098| 1.92964|
| C    | 5.32714| 14.44961| 2.4654|
| H    | 5.62222| 14.31266| 1.42353|
| H    | 4.2441| 14.54127| 2.4857|
| C    | 5.91654| 15.72668| 2.9705|
| C    | 5.47962| 16.27772| 4.17632|
| C    | 5.79705| 17.59672| 4.48665|
| C    | 6.59028| 18.3378| 3.61207|
| H    | 6.78866| 19.37013| 3.85936|
| C    | 7.08141| 17.80891| 2.41879|
| C    | 6.72092| 16.48852| 2.12972|
| H    | 7.02759| 16.05383| 1.18856|
| C    | 5.13207| 18.27864| 5.63885|
| H    | 4.05705| 18.13634| 5.55794|
| C    | 5.32859| 19.35032| 5.57453|
| C    | 7.00316| 18.14596| 7.13323|
| H    | 7.5517| 17.54298| 6.41931|
| H    | 7.18146| 19.20232| 6.92279|
| H    | 7.35818| 17.91861| 8.12992|
| C    | 4.77858| 16.6707| 7.9745|
| H    | 4.81246| 19.72175| 7.67633|
| H    | 5.26877| 18.6096| 8.9384|
| C    | 3.33006| 18.2181| 8.03073|
| H    | 2.80757| 18.74132| 8.83262|
| H    | 2.82184| 18.48544| 7.10942|
| C    | 1.93955| 16.28388| 7.53229|
| C    | 2.0184| 16.47708| 8.46683|
### 15. Cartesian coordinates / Å of [Cr\textsuperscript{III}2L\textsuperscript{4+} (2′, gas phase).

| atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | 4.97368 | 9.7965 | 12.73808 |
| C    | 3.79447 | 9.4227 | 13.37538 |
| C    | 3.85658 | 8.63069 | 14.519 |
| H    | 2.92671 | 8.33445 | 14.98109 |
| C    | 5.06008 | 8.15826 | 15.03863 |
| C    | 6.22333 | 8.52435 | 14.35103 |
| C    | 7.1782  | 8.14089 | 14.68267 |
| C    | 6.19707 | 9.31987 | 13.21075 |
| C    | 7.42996 | 9.49013 | 12.38363 |
| H    | 7.21771 | 9.14919 | 11.37379 |
| H    | 8.22158 | 8.85403 | 12.78378 |
| C    | 8.35404 | 11.29014 | 13.67432 |
| C    | 9.06073 | 10.57385 | 14.09753 |
| H    | 7.45791 | 11.31588 | 14.28245 |
| H    | 8.80626 | 12.27351 | 13.6789 |

### Table S9. Cartesian coordinates / Å of [Cr\textsuperscript{III}2L\textsuperscript{4+} (2′).

| atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | 4.97368 | 9.7965 | 12.73808 |
| C    | 3.79447 | 9.4227 | 13.37538 |
| C    | 3.85658 | 8.63069 | 14.519 |
| H    | 2.92671 | 8.33445 | 14.98109 |
| C    | 5.06008 | 8.15826 | 15.03863 |
| C    | 6.22333 | 8.52435 | 14.35103 |
| C    | 7.1782  | 8.14089 | 14.68267 |
| C    | 6.19707 | 9.31987 | 13.21075 |
| C    | 7.42996 | 9.49013 | 12.38363 |
| H    | 7.21771 | 9.14919 | 11.37379 |
| H    | 8.22158 | 8.85403 | 12.78378 |
| C    | 8.35404 | 11.29014 | 13.67432 |
| C    | 9.06073 | 10.57385 | 14.09753 |
| H    | 7.45791 | 11.31588 | 14.28245 |
| H    | 8.80626 | 12.27351 | 13.6789 |
| C | 9.2081 | 10.79963 | 11.43923 |
| H | 9.85222 | 9.9844 | 11.77928 |
| H | 9.77295 | 11.71465 | 11.57224 |
| C | 8.83459 | 10.56594 | 9.98377 |
| H | 8.4571 | 9.56666 | 9.85389 |
| H | 9.72242 | 10.64573 | 9.35491 |
| C | 6.92498 | 10.815 | 8.48917 |
| H | 6.18061 | 11.51106 | 8.11128 |
| H | 6.42285 | 9.97485 | 8.95674 |
| H | 7.53258 | 10.45988 | 7.65517 |
| C | 8.40784 | 12.67672 | 8.80106 |
| H | 7.61497 | 13.21575 | 8.28665 |
| H | 9.1043 | 12.31953 | 8.0924 |
| C | 9.11573 | 13.57792 | 9.78341 |
| H | 9.95976 | 13.07681 | 10.24495 |
| H | 9.52447 | 14.44713 | 9.2643 |
| C | 8.91403 | 14.45746 | 12.04777 |
| H | 9.48872 | 13.56933 | 12.4621 |
| H | 8.21306 | 14.82626 | 12.78951 |
| C | 6.90844 | 15.25777 | 11.78338 |
| C | 7.45798 | 15.23171 | 10.30543 |
| H | 7.17397 | 15.00701 | 9.28021 |
| H | 8.19696 | 16.03412 | 10.2689 |
| C | 6.24401 | 15.71675 | 11.03386 |
| C | 5.00834 | 15.11673 | 10.77751 |
| C | 3.8338 | 15.77251 | 11.14744 |
| C | 3.91635 | 16.92544 | 11.91913 |
| H | 2.99388 | 17.41956 | 12.18337 |
| C | 5.13007 | 17.46866 | 12.32638 |
| H | 6.28544 | 16.87129 | 11.80675 |
| H | 7.24661 | 17.33525 | 11.98337 |
| C | 2.53069 | 15.34995 | 10.57561 |
| H | 2.07753 | 15.06919 | 9.5355 |
| H | 1.8403 | 16.19119 | 10.59297 |
| C | 1.30638 | 14.69527 | 12.54463 |
| C | H | 0.67838 | 15.57423 | 12.38697 |
| H | 2.13797 | 14.95879 | 13.18898 |
| H | 0.70249 | 13.93149 | 13.02112 |
| C | 0.7142 | 13.82273 | 10.34005 |
| H | 0.28496 | 14.71982 | 9.88579 |
| H | -0.08188 | 13.36341 | 10.9144 |
| C | 1.23486 | 12.89901 | 9.26658 |
| H | 1.97116 | 13.40665 | 8.64788 |
| H | 0.42456 | 12.57834 | 8.60868 |
| C | 2.58362 | 10.97919 | 8.75284 |
| H | 1.85573 | 10.6676 | 8.00203 |
| H | 3.09579 | 10.10695 | 9.1442 |
| H | 3.30901 | 11.64182 | 8.28808 |
| C | 0.87544 | 10.79891 | 10.48066 |
| H | 1.19964 | 9.77625 | 10.31798 |
| H | -0.07456 | 10.90883 | 9.95609 |
| C | 0.67739 | 11.05088 | 11.96641 |
| H | 0.16876 | 11.9873 | 12.1602 |
| H | 0.04361 | 10.26228 | 12.3802 |
| C | 1.79792 | 11.51554 | 14.08645 |
| H | 1.37831 | 12.51203 | 14.13061 |
| H | 2.75888 | 11.51641 | 14.58605 |
| H | 1.1231 | 10.82748 | 14.59859 |
| C | 2.47542 | 9.66455 | 12.71993 |
| C | 1.71104 | 9.07968 | 13.23454 |
| H | 2.53036 | 9.2999 | 11.65786 |
| C | 5.11773 | 7.20258 | 16.22966 |
| C | 3.76241 | 7.07517 | 16.93798 |
| H | 3.39476 | 8.03711 | 17.29971 |
| H | 3.87074 | 6.4208 | 17.80104 |
| H | 3.00559 | 6.6254 | 16.25367 |
| C | 5.50947 | 5.82048 | 15.7066 |
| H | 4.80023 | 5.45156 | 14.9561 |
| H | 5.50025 | 5.09169 | 16.52353 |
| H | 6.5057 | 5.79016 | 15.26273 |
| C | 6.16369 | 7.69604 | 17.24652 |
| H | 7.16568 | 7.74048 | 16.81795 |
| H | 6.20408 | 7.01145 | 18.09249 |
|   |   |   |   |
|---|---|---|---|
| H | 5.90906 | 8.68561 | 17.62841 |
| C | 5.20812 | 18.69276 | 13.23309 |
| C | 3.8288  | 19.08657 | 13.77839 |
| H | 3.3639  | 18.26892 | 14.46376 |
| H | 3.15207 | 19.40754 | 12.98589 |
| C | 5.77383 | 19.88146 | 12.43247 |
| H | 5.83768 | 20.76043 | 13.07319 |
| H | 5.12562 | 20.12574 | 11.59113 |
| H | 6.7711  | 19.67737 | 12.04119 |
| C | 6.12809 | 18.36242 | 14.42292 |
| H | 6.20302 | 19.22468 | 15.08436 |
| H | 7.13768 | 18.10303 | 14.10336 |
| H | 5.7312  | 17.52664 | 15.00025 |
| N | 7.99203 | 10.88276 | 12.29264 |
| N | 7.77628 | 11.51238 | 9.4883  |
| N | 8.1624  | 14.01603 | 10.84872 |
| N | 1.83406 | 14.19845 | 11.25273 |
| N | 1.90281 | 11.70295 | 9.86049 |
| N | 1.98262 | 11.08286 | 12.67798 |
| S | 4.90256 | 10.72508 | 11.23013 |
| S | 4.9182  | 13.51468 | 10.00072 |
| Cr| 6.73009 | 12.31965 | 11.20674 |
| Cr| 3.20193 | 12.43261 | 11.44426 |

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