Deciphering the photophysical kinetics, electronic configurations and structural conformations of Iridium-Cobalt Hydrogen Evolution Photocatalysts

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Experimental Details

Extended X-ray Absorption Fine Structure (EXAFS) Analysis. Athena software\(^1\) was used for data processing. The energy scale for each scan was normalized using cobalt and iridium metal standard. Data in energy space were pre-edge corrected, normalized, de-glitched (if necessary), and background corrected. The processed data were next converted to the photoelectron wave vector (k) space and weighted by \(k^2\). The electron wave number is defined as \(k = [2m(E - E_0)/h^2]^{1/2}\), \(E_0\) is the energy origin or the threshold energy. K-space data were truncated near the zero crossings \(k = 2\) to \(11\) Å\(^{-1}\) for the Co and Iridium complexes’ ground states Co/Ir EXAFS Fourier transformation. The k-space data were transferred into the Artemis Software for curve fitting. In order to fit the data, the Fourier peaks were isolated separately, grouped together, or the entire (unfiltered) spectrum was used. The individual Fourier peaks were isolated by applying a Hanning window to the first and last 15% of the chosen range, leaving the middle 70% untouched. Curve fitting was performed using \textit{ab initio}-calculated phases and amplitudes from the FEFF8\(^2\) program from the University of Washington. \textit{Ab initio}-calculated phases and amplitudes were used in the EXAFS equation (Equation 1),

\[
\chi(k) = S_0^2 \sum_j \frac{N_j}{kR_j^2} f_{\text{eff}}(\pi, k, R_j) e^{-2\sigma^2 k^2} e^{-2R_j/k} \sin(2kR_j + \phi_j(k))
\]  

(Equation 1)

where \(N_j\) is the number of atoms in the \(j^{th}\) shell; \(R_j\) the mean distance between the absorbing atom and the atoms in the \(j^{th}\) shell; \(f_{\text{eff}}(\pi, k, R_j)\) is the \textit{ab initio} amplitude function for shell \(j\), and the Debye-Waller term \(e^{-2\sigma^2 k^2}\) accounts for damping due to static and thermal disorder in absorber-backscatterer distances. The mean free path term \(e^{-2R_j/k}\) reflects losses due to inelastic scattering, where \(\lambda_j(k)\), is the electron mean free path. The oscillations in the EXAFS spectrum are reflected in the sinusoidal term \(\sin(2kR_j + \phi_j(k))\), where \(\phi_j(k)\) is the \textit{ab initio} phase function for shell \(j\). This sinusoidal term shows the direct relation between the frequency of the EXAFS oscillations in k-space and the absorber-backscatterer distance. \(S_0^2\) is an amplitude reduction factor.

The EXAFS equation\(^4\) (Eq. 1) was used to fit the experimental Fourier isolated data (q-space) as well as unfiltered data (k-space) and Fourier transformed data (R-space) using \(N, S_0^2, E_0, R, \) and \(\sigma^2\) as variable parameters (Table S1). \(N\) refers to the number of coordination atoms surrounding Co/Ir for each shell. The quality of fit was evaluated by R-factor and the reduced Chi\(^2\) value. The deviation in \(E_0\) ought to be less than or equal to 10 eV. R-factor less than 2% denotes that the fit is good enough. R-factor between 2 and 5% denotes that the fit is correct within a consistently broad model. The reduced Chi\(^2\) value is used to compare fits as more absorber-backscatter shells are included to fit the data. A smaller reduced Chi\(^2\) value implies a better fit. Similar results were obtained from fits done in k, q, and R-spaces.
Steady-state and time-resolved XAS measurements. Steady-state and time-resolved X-ray absorption spectra were collected at 11 ID-D\textsuperscript{3} beamlines at the Advanced Photon Source using undulator radiation at electron energy 7.71 KeV (Co K-edge) and 11.22 KeV (Ir L\textsubscript{3}-edge) in solvent grade acetonitrile. The samples were circulated through a stainless-steel nozzle into a free-flowing cylindrical jet inside an airtight aluminum chamber, and continuously degassed with nitrogen. This sample handling technique ensures proper sample recovery such that the subsequent laser pulse can hit a “fresh” sample position.

Cooled running water from a chiller was additionally circulated around the jacketed sample flask to prevent heating damage of the complexes by radiation. The X-ray fluorescence signals were collected with two avalanche photodiodes (APDs) positioned at 90° on both sides of the liquid jet, and a combination of Z-1 filters and soller slits with conical geometry were used to reduce the background from elastically scattered X-rays.

The experiments were carried out using the 24 bunch timing mode of APS (in top up mode with a constant 102 mA ring current) which consists of a train of X-rays separated by 153 ns. This mode easily allows for gateable detectors that selects X-ray pulses. This timing mode was suitable for this type of experiments in which the separation between adjacent X-ray pulses was long enough for the Avalanche Photodiode (APD) detector to resolve individual X-ray pulses.

The time-resolved experiments were carried out by pumping the samples at 400 nm wavelength using a regenerative amplified laser with 10 kHz repetition rate 5 ps-FWHM pulse length and laser power of 630 mW at the sample. The X-ray and laser beam was spatially overlapped with an X-ray spot size of 100 μm(V) x 450 μm(H) and laser spot size of 170 μm(V) x 550 μm. With a liquid flow speed of around 4.5 m/s, the pumped laser volume was calculated to move out of the FWHM laser pulse region in around 20 μs. This temporal range ensured that the excited state volume was probed more at the centre and less at the edges where the excitation fraction would be less, due to movement of the sample. Beamline 11 ID-D has an automated data digitization system which allows for all X-ray pulses after laser excitation to be collected. Such a system, together with the larger X-ray beam spot size, was very useful for our experiments, as multiple X-ray pulses after laser excitation were averaged to monitor the dynamics for the formation and decay of the Co(II) transient signal in the nano-microsecond time regime.

The UV-vis measurements of the dyads before and after X-ray and laser exposure were checked after each run to ensure lack of X-ray and laser damage of the complexes. The laser-on XAS of the dyads at both Co K-edge and Ir L\textsubscript{3}-edge energies were further checked scan by scan at every 20 min interval to ensure lack of X-ray radiation and laser-induced damage (Figure S6). The “laser-on” X-ray measurements of the dyads I and II collected over one batch of experiments after laser exposure and over the course of 2.7 hours at Co K-edge and Ir L\textsubscript{3}-edge energies are shown in Figure S6. No decomposition of the dyads was hereby observed, thus ensuring the samples’ integrity.

The delay between the pump and X-ray pulses was adjusted by a programmable delay line (PDL-100A-20NS, Colby Instruments). A Co/Ir metal foil was placed between two ionization chambers downstream to the X-ray beam, and its transmission recorded with each scan for energy calibration.
**Optical Transient Absorption Measurements.** Ultrafast transient absorption spectroscopy was carried out at the Center for Nanoscale materials at Argonne National Laboratory with an amplified Ti-sapphire laser (Spectra Physics, Spitfire Pro) at 1 KHz repetition rate and an automated data acquisition system (Ultrafast Systems, Helios). The Ir dyads and Ir complexes were pumped with 405 nm excitation and typical pulse energy of 300 nJ per pulse, and probed with a super-continuum (Ultrafast systems, Helios) light source. The transient absorption data included a set of two-dimensional data together with kinetics spectra for a probe wavelength of 450 to 750 nm. The temporal chirp in the optical transient absorption data of the probe beam were corrected using the non-resonant response of blank water, and acetonitrile solvent, the latter of which gave an IRF of 400 fs. The samples were degassed with N$_2$ gas and continuously magnetically stirred in a 2 mm cuvette.

**DFT Calculations.** The DFT optimization calculations were performed using the ORCA (Version 5.0) program package developed by Neese$^4$ and co-workers. The geometry optimizations were carried out using the solid-state (XRD) as a starting point. The calculations were carried out using the BP86 exchange-correlation functional$^5$ in combination with the triple zeta valance polarization functions (def2-TZVP)$^6$, and the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ)$^7,8$. The RI$^9$ approximation were used to accelerate Coulomb and exchange integrals for the ground and excited state calculations respectively. The default GRID settings were further used for the self-consistent field iterations and for the final energy evaluation. The calculated structures were confirmed to be minima based on a check of the energies and the absence of imaginary frequencies from frequency calculations carried out on the optimized geometries.

**Time-dependent (TD)-DFT XANES Calculations.** Time-dependent DFT (TD)-DFT calculations for the XANES spectra of the Cu complexes were carried out using the hybrid-DFT functional B3LYP due to its preferred use in predicting spectroscopic features.$^{10}$ The TD-DFT XANES simulations were in this case performed with the B3LYP$^{11,12}$ as functional with the def2-TZVP triple-zeta$^{11,12}$ basis sets together with the ZORA approximation and D3BJ dispersion correction effects with dense integration grids. The def2-TZVP/J auxiliary basis set was also employed. The XANES absorption spectra from the TD-DFT calculations were shifted in energy, by -5 eV relative to the experimental data as previously demonstrated$^{13-15}$, and a broadening of 2.0 eV was applied to all calculated spectra. Up to 150 roots were calculated. The calculated XANES spectrum contains contributions from electric quadrupole, electric dipole and magnetic dipole transitions. All spectra were broadened with a Gaussian line shape of 2.0 eV (FWHM).
Table S1. EXAFS Fits parameters for Co and Ir-based complexes

| Complex | Fit | Region | Shell, N | R, Å | E₀  | ss.² (1₀⁻³) | R-factor | Reduced Chi-square |
|---------|-----|--------|----------|------|-----|-------------|----------|-------------------|
| Co(III) chlorido complex | 1   | I      | Co-N,5   | 1.87 | -8.6| 4.9         | 0.0594   | 1954             |
|         | 2   | I      | Co, N-5, Co-Cl, 1 | 1.84 | 2.15|-13         | 0.55     | 0.0221           | 515     |
|         | 3   | I,II   | Co-N,5, Co-Cl, 1, Co-C, 10 | 1.85 | 2.16,-9.4 | 1.8 | 0.50 | 9.3 | 0.0135 | 246   |
| Ir(ppy)₂-L | 4   | I      | Ir-C/N,6 | 2.00 | -0.74| 5.9 | 0.0145 | 132 |
|         | 5   | I,II   | Ir-C/N,6, Ir-C, 4, IrC, 8 | 2.00 | 2.75 | -3.0 | 6.5 | 5.5 | 2.9 | 0.0202 | 136 |
| Ir(piq)₂-L | 6   | I      | Ir-C/N,6 | 2.01 | -1.2 | 7.5 | 0.0165 | 147 |
|         | 7   | I,II   | Ir-C/N,6, Ir-C, 4, IrC, 8 | 1.98 | 2.67, -4.8 | 7.8 | 3.5 | 2.6 | 0.0157 | 108 |

* The amplitude reduction factor S₀² was fixed to 0.8
Figure S1 A. Normalized Co K-edge EXAFS for Co$^{\text{III}}$ complex in dyads I and II (black). B. Normalized Ir L$_3$-edge EXAFS for Ir(ppy)$_2$-L (red) and C. Ir(piq)$_2$-L (green) in dyads I and II respectively.
Figure S2. Fourier transforms of $k^2$-weighted EXAFS for A. 1 mM Co(III) complex in dyads I and II (solid black line) and its corresponding fit (Fit 3, Table S1), for B. 1 mM Ir(ppy)$_2$-L complex (Dyad I) (red solid line), and its corresponding fit (Fit 5, Table S1) and C. 1 mM Ir(piq)$_2$-L complex (Dyad II) (green solid line) and its corresponding fit (Fit 7, Table S1).

Figure S3. Simulated EXAFS spectra for Co$^{III}$ chloro complex in dyads I and II. Atomic coordinates were obtained from single crystal X-ray diffraction structure of [LCo$^{III}$Cl]$^+$ (solid black line)$^{16}$ and from DFT simulations (dashed black line)
Figure S4. Stacked spectra corresponding to a series of time delays between laser and X-ray pulses of A. dyad I and B. dyad II. These measurements were carried out for a range of averaged time delays from 0 to 18.4 µs. The dotted lines represent the raw data and the solid lines represent a smoothening of the spectrum.

Figure S5. Pump-probe time delay scans recorded at 11.2 keV of A. Ir(ppy)$_2$-L and B. Ir(piq)$_2$-L complexes with triethanolamine in the absence of the Co$^{III}$ catalyst and tetrafluoroboric acid proton source. Kinetic fittings of the Ir $^3$MLLCT state with the electron donor triethanolamine ($T_1$) together with the back electron transfer times ($T_2$) in the case of complex Ir(piq)$_2$-L are indicated.
Figure S6. “Laser-on” scans of dyads I and II at Co K-edge energy of A. Dyad I B. Dyad II and at Ir L₃-edge of C. Dyad I, D. Dyad II. No change is hereby observed in the XANES spectra of one batch of sample over the course of 2.7 hrs indicating their intact nature and lack of decomposition.
**Figure S7** A. Normalized Co K-edge XANES for Co$^{\text{III}}$ complex (black) and Co$^{\text{III}}$ complex shifted by -1 eV (in red). B. Experimental difference spectrum between black and red spectrum shown in **Figure S4** A. A difference spectrum with a peak energy of 7720 eV is observed showing that the K-edge of the Co centre shifts to lower energy and confirming the formation of Co$^{\text{II}}$ from Co$^{\text{III}}$. 
Appendix

DFT optimized coordinates of using the BP-86\textsuperscript{5} functional, and the atom-pairwise Grimme dispersion correction with the Becke-Johnson damping scheme (D3BJ)\textsuperscript{7}.

[LCo\textsuperscript{III}Cl]\textsuperscript{2+} octahedral complex

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| Co   | 23.056504 | 7.777308 | 17.785380 |
| O    | 21.133961  | 8.210469  | 19.810294  |
| O    | 23.359639  | 9.050204  | 15.284206  |
| O    | 22.812090  | 6.480054  | 20.333957  |
| O    | 25.108790  | 7.392870  | 15.815900  |
| N    | 21.902887  | 6.436150  | 16.947589  |
| N    | 21.555748  | 8.581747  | 18.620658  |
| N    | 22.656127  | 9.001953  | 16.392380  |
| N    | 23.518457  | 6.571442  | 19.200757  |
| N    | 24.627794  | 7.009856  | 17.007008  |
| C    | 19.820890  | 10.317188 | 18.423281  |
| H    | 19.494455  | 9.819195  | 19.301944  |
| H    | 20.045502  | 10.422881 | 17.650909  |
| H    | 20.130728  | 11.331388 | 18.720904  |
| N    | 22.987018  | 9.534782  | 17.917094  |
| C    | 21.022254  | 9.777969  | 16.630309  |
| C    | 21.173937  | 10.829240 | 15.669665  |
| H    | 21.948427  | 10.980694 | 14.909620  |
| H    | 20.983734  | 11.780016 | 16.187477  |
| H    | 20.241322  | 10.539036 | 15.159357  |
| C    | 25.133050  | 4.891740  | 20.019472  |
| H    | 24.528566  | 4.929730  | 20.931035  |
| H    | 26.173872  | 5.142692  | 20.271547  |
| H    | 25.128932  | 3.860497  | 19.633611  |
| C    | 24.590359  | 5.847928  | 19.010084  |
| C    | 25.240906  | 6.106094  | 17.724700  |
| C    | 26.511084  | 5.441622  | 17.309719  |
| H    | 26.779066  | 5.747364  | 16.293952  |
| H    | 26.414999  | 4.346007  | 17.345256  |
| H    | 27.332228  | 5.720268  | 17.987955  |
| C    | 20.268495  | 4.511895  | 15.758818  |
| C    | 20.079548  | 4.886312  | 17.088908  |
| H    | 19.294087  | 4.442421  | 17.699410  |
| C    | 20.910781  | 5.849472  | 17.650896  |
| H    | 20.790076  | 6.175730  | 18.682735  |
| C    | 22.084927  | 6.083308  | 15.657505  |
| H    | 22.883832  | 6.593261  | 15.122560  |
| C    | 21.289361  | 5.127506  | 15.035058  |
| H    | 21.479054  | 4.877809  | 13.991904  |
| H    | 22.040704  | 7.282057  | 20.200533  |
| Element | X Position | Y Position | Z Position |
|---------|------------|------------|------------|
| H       | 24.392369  | 8.197634   | 15.517943  |
| H       | 19.631416  | 3.758476   | 15.294681  |
| Cl      | 24.359544  | 9.333316   | 18.738533  |

$[\text{LCo}^{\text{III}}\text{CH}_3\text{CN}]^{3+}$ octahedral complex

| Element | X Position | Y Position | Z Position |
|---------|------------|------------|------------|
| Co      | 23.209160  | 7.662558   | 17.811237  |
| O       | 21.427138  | 8.356376   | 19.872275  |
| O       | 23.634264  | 8.884637   | 15.308775  |
| O       | 22.872109  | 6.399391   | 20.380403  |
| O       | 25.127261  | 6.950838   | 15.776988  |
| N       | 21.859009  | 6.506693   | 17.017620  |
| N       | 21.827362  | 8.660040   | 18.666501  |
| N       | 22.931241  | 8.915470   | 16.408959  |
| N       | 23.527251  | 6.369104   | 19.211788  |
| N       | 24.616028  | 6.635684   | 16.975468  |
| C       | 20.261928  | 10.546052  | 18.447863  |
| H       | 19.956000  | 10.230143  | 19.450029  |
| H       | 19.387816  | 10.510746  | 17.780630  |
| H       | 20.598341  | 11.592558  | 18.492481  |
| C       | 21.349039  | 9.654296   | 17.948005  |
| C       | 21.986678  | 9.800103   | 16.644212  |
| C       | 21.647048  | 10.843877  | 15.633174  |
| H       | 22.557475  | 11.368496  | 15.310284  |
| H       | 20.930616  | 11.571552  | 16.028710  |
| H       | 21.217913  | 10.380250  | 14.732040  |
| C       | 24.810056  | 4.390316   | 19.936109  |
| H       | 24.435347  | 4.634221   | 20.935443  |
| H       | 25.899948  | 4.261653   | 19.974465  |
| H       | 24.376286  | 3.423963   | 19.634326  |
| C       | 24.433986  | 5.460782   | 18.968401  |
| C       | 25.067231  | 5.612343   | 17.650348  |
| C       | 26.144865  | 4.710858   | 17.151757  |
| H       | 26.226189  | 4.783376   | 16.061714  |
| H       | 25.947667  | 3.669269   | 17.437419  |
| H       | 27.119581  | 4.992289   | 17.581236  |
| C       | 19.952719  | 4.816423   | 15.891079  |
| C       | 19.914365  | 5.129337   | 17.249455  |
| H       | 19.144537  | 4.726137   | 17.905965  |
| C       | 20.879445  | 5.976467   | 17.781630  |
| H       | 20.872794  | 6.250246   | 18.834129  |
| C       | 21.895687  | 6.217902   | 15.698679  |
| H       | 22.686318  | 6.683466   | 15.114373  |
| C       | 20.960767  | 5.376291   | 15.107149  |
| H       | 21.034098  | 5.171389   | 14.039902  |
| H       | 22.220952  | 7.274606   | 20.266528  |
| Atomic Symbol | X   | Y   | Z   |
|---------------|-----|-----|-----|
| H             | 24.544320 | 7.831700 | 15.489189 |
| N             | 24.472861 | 8.817529 | 18.568415 |
| H             | 19.208669 | 4.152251 | 15.450877 |
| C             | 25.240123 | 9.547350 | 19.032536 |
| C             | 26.198353 | 10.464727 | 19.609813 |
| H             | 25.694990 | 11.397550 | 19.899076 |
| H             | 26.984482 | 10.694064 | 18.877104 |
| H             | 26.657079 | 10.016628 | 20.501827 |

**[LCo^{II}Cl]^+ octahedral complex**

| Atomic Symbol | X   | Y   | Z   |
|---------------|-----|-----|-----|
| Co            | 23.296993 | 7.549305 | 17.902322 |
| O             | 21.366522 | 8.017348 | 19.948352 |
| O             | 23.385691 | 8.673771 | 15.256319 |
| O             | 23.139046 | 6.333749 | 20.510952 |
| O             | 25.137596 | 6.964176 | 15.799993 |
| N             | 21.884407 | 5.936952 | 17.000704 |
| N             | 21.770725 | 8.316997 | 18.730574 |
| N             | 22.743466 | 8.623672 | 16.453642 |
| N             | 23.782410 | 6.394144 | 19.315340 |
| N             | 24.766335 | 6.700041 | 17.038792 |
| C             | 19.869236 | 9.865036 | 18.467640 |
| H             | 19.372496 | 9.225454 | 19.210077 |
| H             | 19.173846 | 10.083264 | 17.644815 |
| H             | 20.109478 | 10.817982 | 18.970728 |
| C             | 21.099373 | 9.173056 | 17.977176 |
| C             | 21.679203 | 9.361392 | 16.658360 |
| C             | 21.129042 | 10.302071 | 15.633934 |
| H             | 21.894353 | 10.502432 | 14.875120 |
| H             | 20.817864 | 11.250387 | 16.094981 |
| H             | 20.248107 | 9.874186 | 15.125678 |
| C             | 25.411713 | 4.752265 | 20.160331 |
| H             | 25.197076 | 5.167125 | 21.153920 |
| H             | 26.497281 | 4.639104 | 20.038227 |
| H             | 24.960273 | 3.746277 | 20.119284 |
| C             | 24.844632 | 5.656142 | 19.112005 |
| C             | 25.411833 | 5.818383 | 17.782519 |
| C             | 26.618454 | 5.085994 | 17.290861 |
| H             | 26.657743 | 5.166954 | 16.196866 |
| H             | 26.596150 | 4.024020 | 17.579439 |
| H             | 27.549546 | 5.521628 | 17.692718 |
| C             | 19.734284 | 5.373665 | 15.277233 |
| C             | 19.517742 | 5.659080 | 16.629801 |
| H             | 18.510983 | 5.671065 | 17.051411 |
| C             | 20.610024 | 5.929861 | 17.450165 |
| H             | 20.480805 | 6.169155 | 18.507873 |
| C             | 22.088712 | 5.647788 | 15.696916 |
[LCo$^{II}$CH$_3$CN]$^{2+}$ octahedral complex

Co  23.079043  7.571296  17.739524
O  21.126045  8.016721  19.757972
O  23.521485  9.108183  15.332716
O  22.800996  6.232351  20.269414
O  25.160346  7.257449  15.807763
N  21.874422  6.222000  16.770713
N  21.649019  8.445479  18.632398
N  22.814276  8.975761  16.494413
N  23.550691  6.415428  19.157992
N  24.698955  6.893045  16.996454
C  20.071794 10.328464  18.628795
H  19.267742  9.660161  18.968499
H  19.662639 11.051488  17.913005
H  20.419385 10.876676  19.519377
C  21.864561  9.833990  16.784329
C  21.522900 11.002731  15.919600
H  22.261389 11.105772  15.117948
H  21.495802 11.930725  16.509374
H  20.529355 10.878632  15.460280
C  25.179132  4.803437  20.055328
H  24.915395  5.178678  21.052504
H  26.267184  4.686290  19.983304
H  24.721416  3.806085  19.952685
C  24.667262  5.742456  19.013591
C  25.336776  6.011292  17.747426
C  26.617201  5.369951  17.324461
H  26.754384  5.519126  16.246878
H  26.617724  4.293409  17.547926
H  27.483459  5.813662  17.841965
C  20.223189  4.407796  15.440103
C  19.892846  4.871336  16.714217
H  18.986634  4.539871  17.220465
C  20.740440  5.776857  17.347239
H  20.522770  6.169430  18.342010
C  22.197692  5.773085  15.541700
H  23.127935  6.158216  15.120868
C      21.398561    4.869518   14.846502
H      21.701557    4.537975   13.853896
H      22.037528    6.992781   20.152433
H      24.254007    8.330691   15.436913
N      19.576568    3.700192   14.919623
C      24.712185    9.452813   19.363899
C      25.378537    9.684889   18.438255
C      26.199338    9.956041   17.271841
H      25.720371   10.724583   16.650046
H      26.292191    9.038459   16.669022
H      27.194674   10.304495   17.577716

[Co^{II}]^{2+} square bypiramidal complex

Co     22.928691    7.628737   17.699868
O      21.026385    8.221884   19.780234
O      23.281172    8.965761   15.213150
O      22.656252    6.380248   20.242438
O      25.051520    7.290665   15.779682
N      21.750943    6.218998   16.826902
N      21.526215    8.561253   18.563610
N      22.620605    8.938496   16.352557
N      23.408109    6.521535   19.170829
N      24.559070    6.963158   17.002087
C      19.886347   10.405137   18.422541
H      19.407561    9.904782   19.270632
H      19.138909   10.593805   17.639053
H      20.254272   11.385041   18.766452
C      21.007601    9.568471   17.899998
C      21.644428    9.793490   16.609083
C      21.254277   10.868971   15.649953
H      22.111774   11.109571   15.092833
H      20.921699   11.774449   16.174684
H      20.431784   10.546432   14.989250
C      25.042749    4.924652   20.086826
H      24.754305    5.314133   21.072223
H      26.133497    4.817392   20.037593
H      24.598659    3.919224   19.999293
C      24.535767    5.845430   19.026875
C      25.199642    6.098956   17.755374
C      26.481406    5.451071   17.345362
H      26.616311    5.540284   16.261775
H      26.492764    4.389917   17.630026
H      27.342476    5.933662   17.834828
C      20.175581    4.255907   15.619575
C      20.250990    4.355124   17.009444
H      19.701168    3.673186   17.657919
C 21.047442 5.346567 17.576496
H 21.142497 5.457577 18.658606
C 21.677524 6.127913 15.483615
H 22.259100 6.860550 14.920787
C 20.903427 5.161711 14.846972
H 20.877808 5.127973 13.757492
H 21.686639 7.417304 20.077933
H 24.346061 8.041098 15.447872

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