

## Are There Single-Well Hydrogen Bonds in Pyridine-Dichloroacetic Acid Complexes?

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Electronic Supplementary Information

### EXPERIMENTAL DETAILS

**Materials.** All pyridines, dichloroacetic acid, and dichloroacetic anhydride were purchased from Aldrich Chemical Company. Pyridines were stored over activated 4Å molecular sieves under dry N<sub>2</sub> for several days prior to use. NMR solvents CD<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>3</sub> and 1-mL ampoules of H<sub>2</sub><sup>18</sup>O (97.6 atom% <sup>18</sup>O) were purchased from Cambridge Isotope Labs.

**Preparation of Cl<sub>2</sub>CHCOOH-<sup>18</sup>O<sub>2</sub>.** Dichloroacetyl chloride (0.5 mL, 5 mmol) was stirred in an ice bath with 0.3 mL H<sub>2</sub><sup>18</sup>O (16 mmol) for 1 hr, then warmed to 25°C and stirred. Incorporation of <sup>18</sup>O label was monitored by mass spectrometry. After 48 hr the peaks of mono-<sup>18</sup>O and di-<sup>18</sup>O<sub>2</sub> acids had nearly equal intensities, and the ratio did not change further. The stirring was stopped and water and HCl were evaporated under reduced pressure (<1 mm Hg) for 24 hr. The extent of labeling was confirmed by the <sup>13</sup>C NMR spectrum of a 2:1 mixture with unlabeled dichloroacetic acid in CDCl<sub>3</sub>, which showed three peaks of nearly the same intensity.

**Preparation of NMR Samples.** Samples were prepared under inert atmosphere using syringe transfer techniques. Pyridine or a substituted pyridine (1.2 mmol) was added to dichloromethane-*d*<sub>2</sub> (1 g). Dichloroacetic acid-<sup>18</sup>O<sub>2</sub> (10 uL of 1:1 mixture with dichloroacetic acid-<sup>18</sup>O, 0.06 mmol each) and dichloroacetic acid (5 uL, 0.06 mmol) were added to the solution. To scavenge any adventitious water, dichloroacetic anhydride (9 uL, 0.06 mmol) was added and allowed to react at room temperature at least 30 minutes before recording spectra. This caused some scrambling and dilution of the label, but the <sup>13</sup>C NMR signal of Cl<sub>2</sub>CHCOOH-<sup>18</sup>O<sub>2</sub> was still resolvable. The samples were deoxygenated with N<sub>2</sub> and the same sample was used for <sup>1</sup>H and <sup>13</sup>C spectra at all temperatures.

**Instrumentation.** Mass spectra were obtained using Q-TOF/MS, ESI negative ion mode. NMR Spectra were recorded on a JEOL-500 FT-NMR spectrometer operating at a <sup>13</sup>C frequency of 125.823 MHz. The probe (QNP probe) was double tuned to <sup>1</sup>H and <sup>13</sup>C. Low-temperature spectra were obtained using liquid N<sub>2</sub> coolant and a variable-temperature controller. Temperatures were calibrated from the chemical shifts of a methanol sample. The spectra were recorded with sample spinning at 18 Hz, spectral widths of 200 ppm, 30K to 60K data points, and fourfold zero-filling. The quintet of CD<sub>2</sub>Cl<sub>2</sub> (δ 54 ppm) served as an internal standard for <sup>13</sup>C chemical shifts, although the small separation between carboxyl <sup>13</sup>C-<sup>18</sup>O and <sup>13</sup>C-<sup>16</sup>O signals was the isotope shift of interest.