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Repper, S.E., Haynes, A. orcid.org/0000-0002-6854-1618, Ditzel, E.J. et al. (1 more author) (2017) Infrared spectroscopic study of absorption and separation of CO using copper(I)-containing ionic liquids. Dalton Transactions, 46 (9). pp. 2821-2828. ISSN 1477-9226

https://doi.org/10.1039/C6DT04816A

Supplementary Information

Infrared spectroscopic study of absorption and separation of CO using copper(I)-containing ionic liquids

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Figures S1-S3: Data from high pressure IR experiments for [$C_n$mim][CuX_2] + CO reactions.

Figures S4-S5: UV/vis spectra of solutions of Cu(II) and Cu(I) salts in $MeNO_2$.

Figures S6-S7: Data from gas phase IR measurements for determination of headspace CO content.

Synthesis of 1-alkyl-3-methylimidazolium halide salts

HPIR spectroscopic data for CO uptake experiments

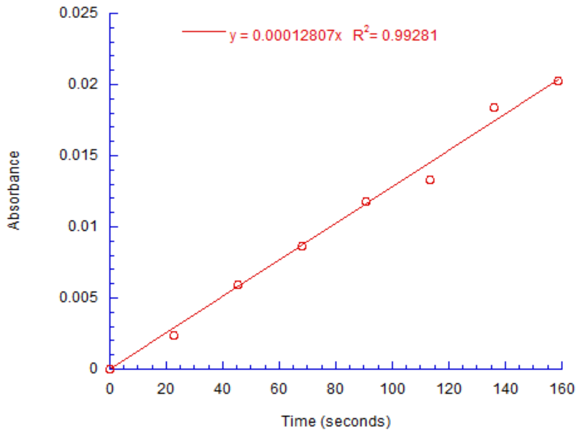

Figure S1. Plot of IR absorbance (2076 cm^{-1}) vs. time for first 160 s of CO uptake by $[C_6mim][CuCl_2]$ at 25 °C (stirrer speed 428 rpm) with initial *p*CO = 8 bar.

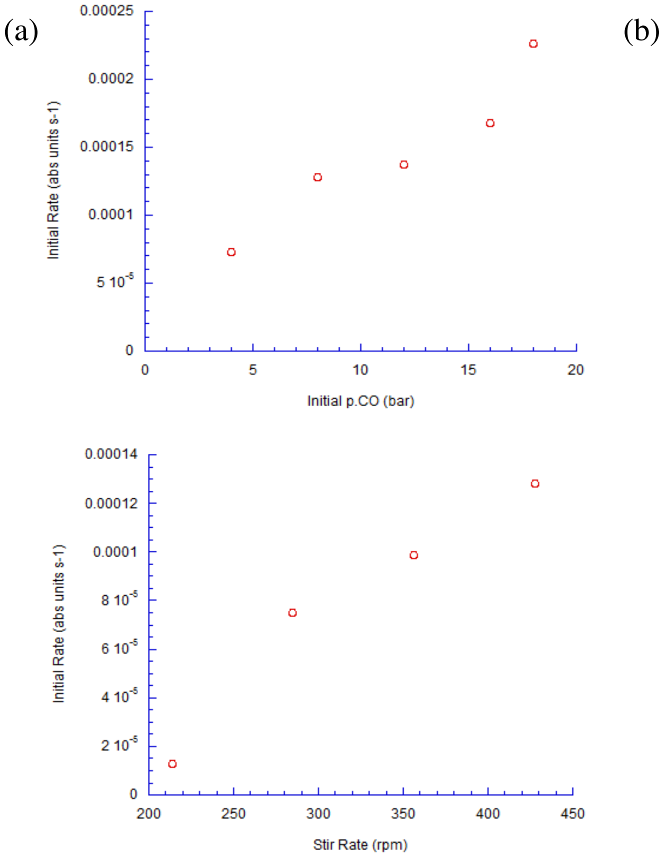

Figure S2. Initial rate of CO uptake for [C_6mim][$CuCl_2$] at 25 °C (from slopes of absorbance vs. time plots, e.g. Fig S1) (a) vs. initial CO pressure (with stirrer speed 428 rpm) and (b) vs. stir rate (with initial pCO = 8 bar).

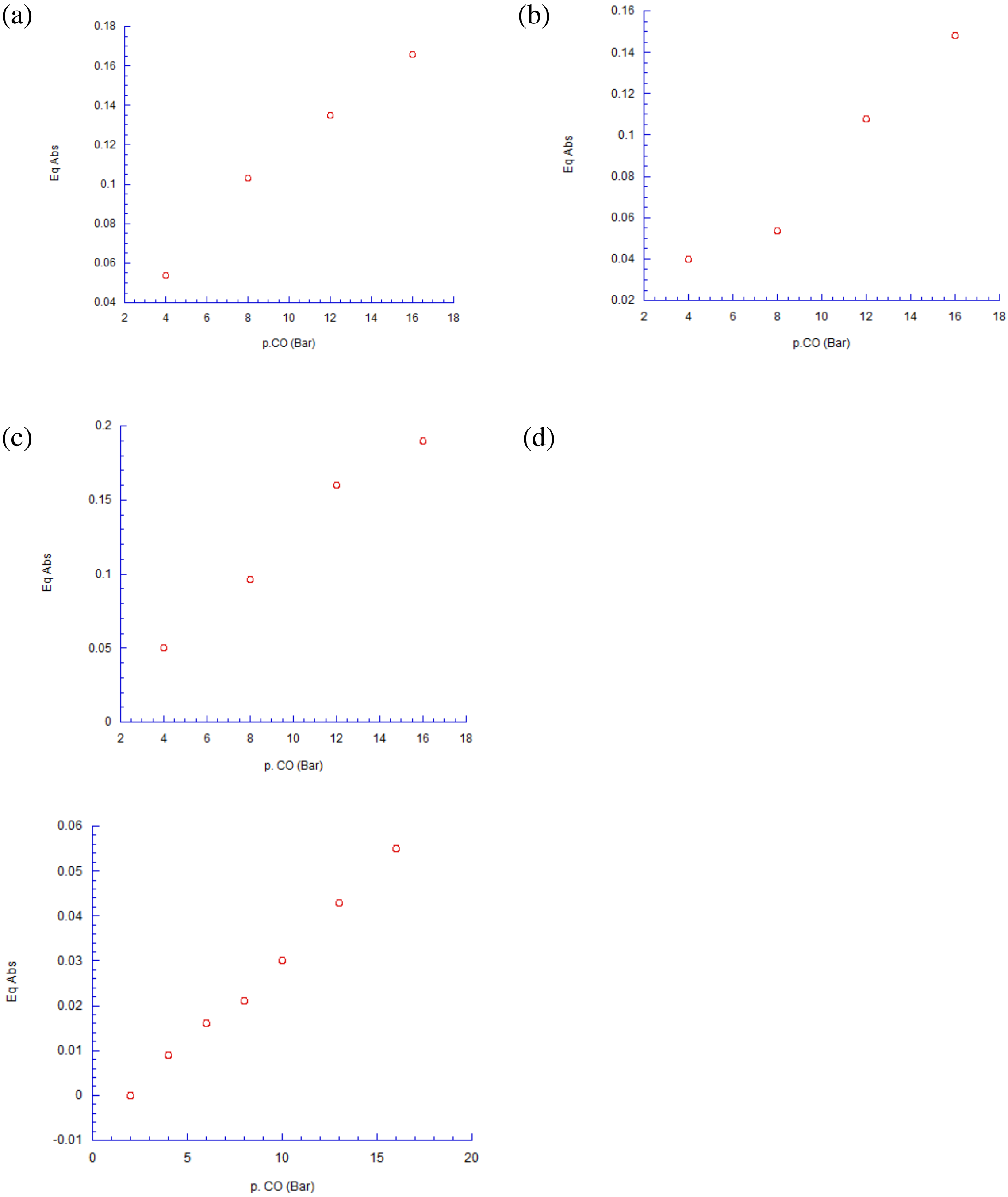

Figure S3. Plots of equilibrium ν(CO) intensity vs. initial CO pressure for CO uptake at 25 °C by (a) [C_2mim][$CuBr_2$]; (b) [C_4mim][$CuBr_2$]; (c) [C_6mim][$CuBr_2$]; (d) [C_6mim][CuI_2].

UV/visible spectroscopic analysis for trace Cu(II)

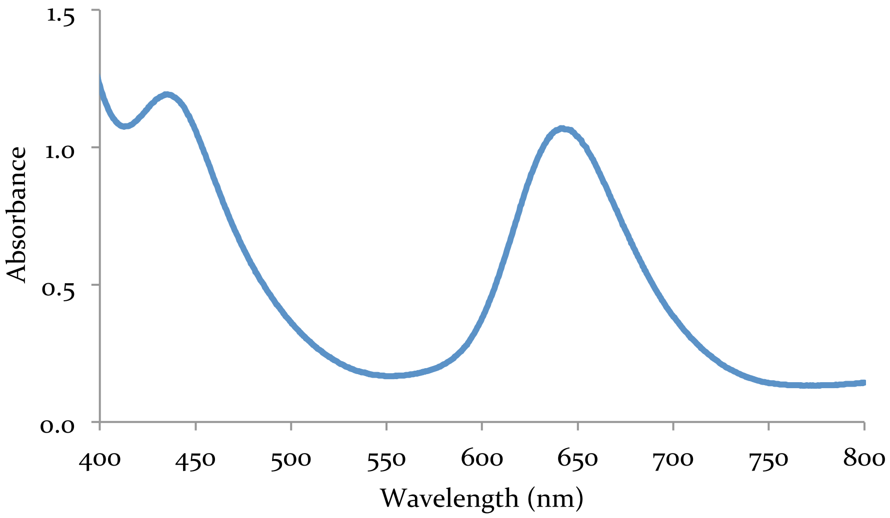

Figure S4. UV/vis spectrum of a 0.001 M solution of a 1:1 mixture of $[C_6mim]Br$ and $CuBr_2$ in CH_3NO_2, showing strong absorptions due to Cu(II).

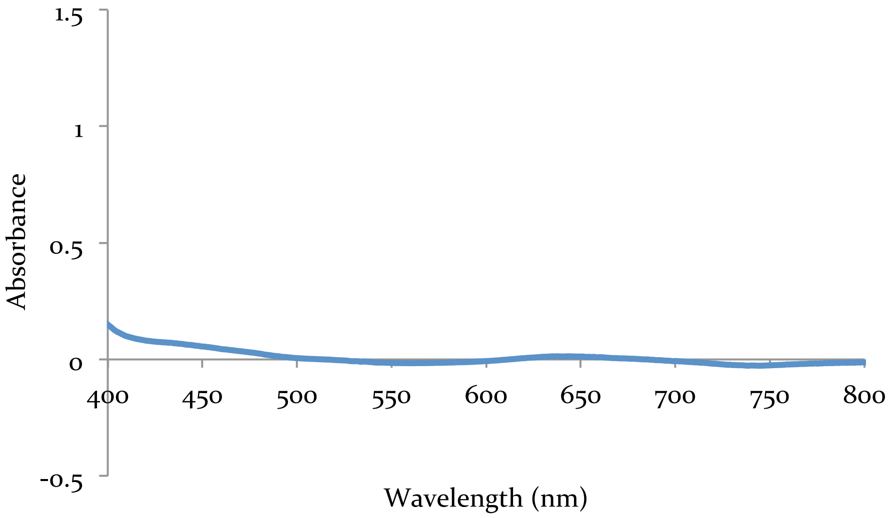

Figure S5. UV/vis spectrum of a 0.01 M solution of $[C_6mim][CuBr_2$ in CH_3NO_2. Note the very weak absorptions due to trace Cu(II) despite the 10x higher Cu concentration compared to Figure S4. Estimated Cu(II) content is <0.1% of total Cu.

Gas-phase IR data for quantification of CO content of gas mixtures

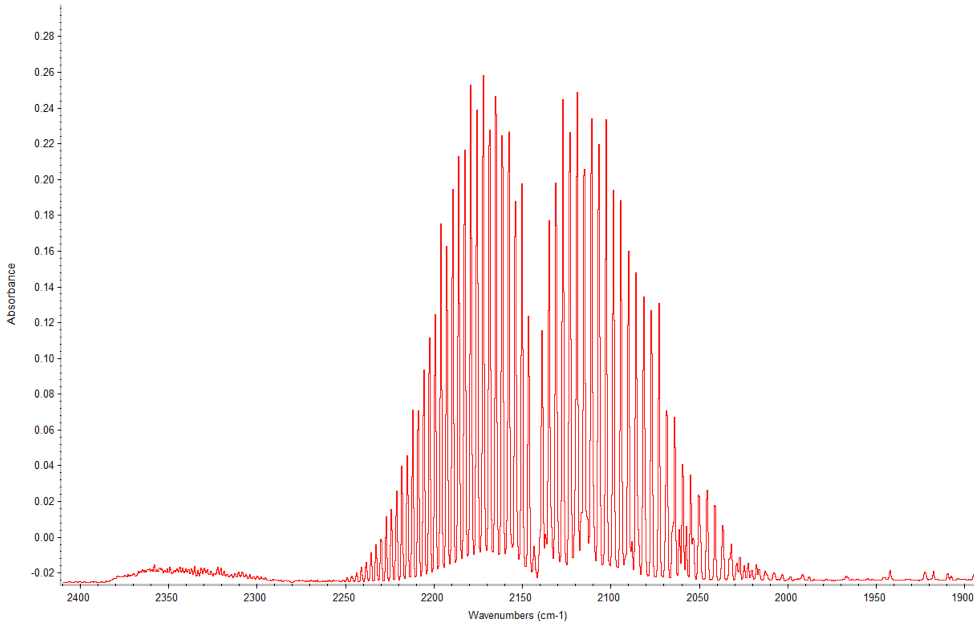

Figure S6. Example gas phase IR spectrum (ν(CO) region) of CO/H_2 mixture in 10 cm gas cell.

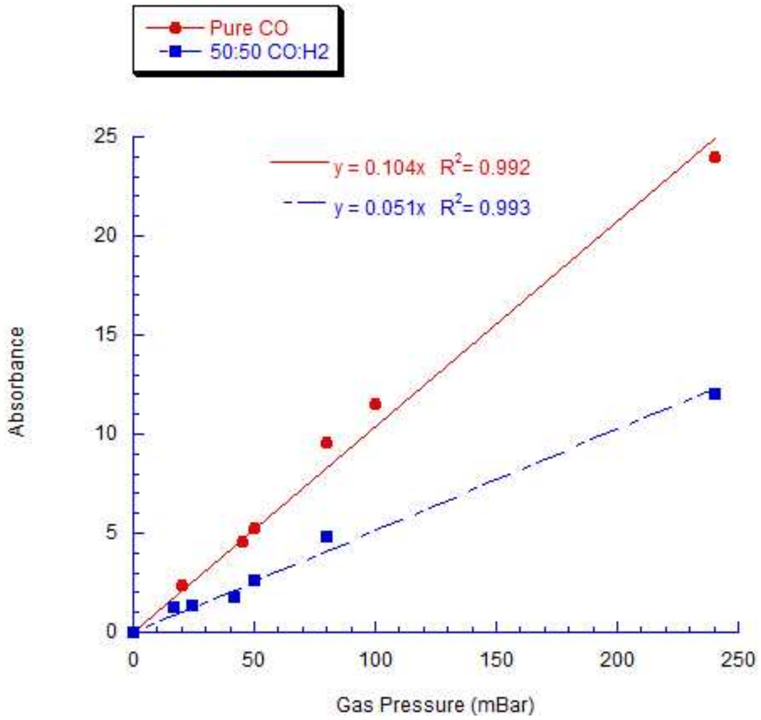

Figure S7. Beer-Lambert calibration plots for pure CO and 1:1 CO:H_2 in 10 cm gas cell. Absorbances are integrated intensities over frequency range 2250-1975 cm^{-1}.

Synthesis of 1-alkyl-3-methylimidazolium halide salts

The synthetic procedure for the 1-alkyl-3-methylimidazolium halide salts was adapted from similar methods reported in the literature.[1, 2] In a typical procedure, 1-methylimidazole or 1,2-dimethylimidazole (~ 0.250 mol) was placed into a degassed and dried round bottom flask under N_2. In the case of the chloride and bromide salts, the alkyl halide precursor was added in excess (~ 1.2 equivalents) and the reaction mixture heated to 80-90 ºC overnight, with the exception being reactions involving the low-boiling bromoethane, which were carried out at 40 ºC. For the iodide salts, 1 equivalent of alkyl iodide was added dropwise at 0 ºC over approximately 20-30 minutes. The reaction vessel was wrapped in foil to prevent the light-induced formation of I_2. The reaction mixture was then stirred at room temperature overnight. ^{1}H NMR spectroscopy was used to assess complete reaction of the 1-methylimidazole. If required, a further 0.1 equivalents of the alkyl halide was added and the reaction allowed to continue for a further 6 hours under the same conditions as previously used. Unreacted alkyl halide was removed under reduced pressure and the product was dried under vacuum at 80 ºC for at least 4 h. All the products were collected either as hygroscopic solids or liquids and were analysed by ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, electrospray mass spectrometry (ES^+ and ES^-) and CHN elemental analysis.

1-hexyl-3-methylimidazolium chloride [C_6mim]Cl pale yellow viscous liquid (36.65 g, 96 %).

^{1}H NMR (250 MHz, $CDCl_3$) δ/ppm, 0.75 (3H, t, 6.9 Hz), 1.15-1.30 (6H, m), 1.80 (2H, m), 4.05 (3H, s), 4.22 (2H, t, 7.4 Hz), 7.46 (1H, s), 7.65 (s, 1H), 10.50 (1H, s)

^{1}H NMR (250 MHz, CD_3NO_2) δ/ppm, 0.89 (3H, t, 6.9 Hz), 1.22-1.42 (6H, m), 1.94 (2H, m), 4.02 (3H, s), 4.30 (2H, t, 7.4 Hz), 7.51 (1H, s), 7.54 (s, 1H), 9.41 (1H, s)

^{13}C NMR (250 MHz, $CDCl_3$), 13.8, 22.2, 25.7, 30.1, 30.9, 36.3, 49.8, 121.9, 123.8, 137.5

TOF MS (ES^+): m/z 167 ([C_6mim]$^+$)

Elemental analysis, calculated for $C_{10}H_{19}N_2Cl$: C 59.22% H 9.38% N 13.83%, found:

C 57.88% H 9.71% N 13.76%

1-ethyl-3-methylimidazolium bromide [C_2mim]Br white crystalline solid (47.96 g, 96 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm, 1.6 (3H, t, 7.4Hz), 4.1 (3H, s), 4.40 (2H, q, 7.4Hz), 7.50 (1H, s), 7.52 (1H, s), 10.43 (1H, s)

^{13}C NMR (250 MHz, $CDCl_3$) δ/ppm, 15.57, 36.53, 45.04, 122.01, 123.64, 136.50

TOF MS (ES^+); m/z 111 ($[C_2mim]^+$), (ES^-); m/z 79 ($[Br]^-$)

Elemental analysis, calculated for $C_6H_{11}N_2Br$: C 37.72% H 5.76% N 14.67%, found: C 37.03% H 5.84% N 14.21%

1-butyl-3-methylimidazolium bromide $[C_4mim]Br$ yellow viscous liquid (26.91 g, 98 %).

^{1}H NMR (250 MHz, $CDCl_3$) δ/ppm, 0.9 (3H, t, 7.4Hz), 1.15 (2H, m), 1.7 (2H, m), 3.90 (3H, s), 4.15 (2H, t, 7.3Hz), 4.44 (1H, s), 7.55 (1H, s), 10.10 (1H, s)

^{13}C NMR (250 MHz, $CDCl_3$) δ/ppm, 13.2, 19.2, 32.1, 36.7, 49.7, 122.1, 123.7, 136.9

TOF MS (ES^+), m/z 139 ($[C_4mim]^+$), (ES^-); m/z 79 ($[Br]^-$)

Elemental analysis, calculated for $C_8H_{15}N_2Br$: C 43.86% H 6.85% N 12.79%, found: C 43.09% H 6.85% N 12.53%

1-hexyl-3-methylimidazolium bromide $[C_6mim]Br$ pale yellow liquid (29.74g, 96 %).

^{1}H NMR (250 MHz, $CDCl_3$) δ/ppm, 0.75 (3H, m), 1.1-1.3 (6H, m), 1.7-1.8 (2H, m), 4.0 (3H, s), 4.2 (2H, t, 7.3Hz), 7.4 (1H, s), 7.6 (1H, s), 9.88 (1H, s)

^{1}H NMR (250 MHz, CD_3NO_2) δ/ppm, 0.89 (3H, t, 6.9Hz), 1.2-1.4 (6H, m), 1.95 (2H, m), 4.01 (3H, s), 4.3 (2H, t, 7.3Hz), 7.53 (1H, s), 7.55 (1H, s), 9.22 (1H, s)

^{13}C NMR (250 MHz, $CDCl_3$) δ/ppm, 13.9, 22.1, 25.5, 30.25, 31.0, 36.75, 50.0, 122.0, 123.7, 137.0

TOF MS (ES^+); m/z 167 ($[C_6mim]^+$), (ES^-); (m/z) 79 ($[Br]^-$)

Elemental analysis, calculated for $C_{10}H_{19}N_2Br$: C 48.60% H 7.70% N 11.34%, found: C 47.28% H 7.73% N 11.07%

1-hexyl-3-methylimidazolium iodide $[C_6mim]I$, was isolated as a pale yellow liquid (yield = 31.19 g, 83 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm, 0.75 (3H, m), 1.1-1.3 (6H, m), 1.85 (2H, m), 4.00 (2H, s), 4.28 (2H, t, Hz), 7.48 (1H, s), 7.58 (1H, s), 9.85 (1H, s)

^{1}H NMR (250 MHz, CD_3NO_2) δ/ppm, 0.90 (3H, t, 6.9 Hz), 1.3-1.4 (6H, m), 1.94 (2H, m), 4.02 (2H, s), 4.29 (2H, t, 7.3Hz), 7.51 (1H, s), 7.55 (1H, s), 8.89 (1H, s)

^{13}C NMR (250 MHz, $CDCl_3$) δ/ppm, 13.79, 22.15, 25.60, 30.01, 30.84, 37.00, 49.49, 122.34, 123.82, 136.25

TOF MS (ES^+); m/z 167 ($[C_6mim]^+$), (ES^-); (m/z) 127 ($[I]^-$)

Elemental analysis, calculated for $C_{10}H_{19}N_2I$: C 40.30% H 6.5% N 9.5%, found: C 40.30% H 7.05% N 9.14%

References

1. S. Liu, C. Xie, S. Yu and F. Liu, *Cat. Comm.*, 2009, **10**, 986.
2. S. V. Dzyuba and R. A. Bartsch, *J. Heterocycl. Chem.*, 2001, **38**, 265.