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$[\mathrm{Cu(CO)}_n]^+$ Complex Ions in the Solid State ($n = 1, 2, 3$)

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Carbonyl complexes of Cu(I) are important chemical species from several points of view. They are probably involved as intermediates in the large-scale industrial transformation of CO to CH_3OH using Cu-promoted ZnO catalysts.[2] They may be involved as intermediates in the heterogeneous Cu-catalyzed low-temperature water gas shift reaction[3] and the homogeneous Cu(I)-catalyzed production of carboxylic acids from alkenes.[4] They are formed when CO is absorbed by supported or soluble Cu(I) salts, processes that are used to remove CO from a variety of industrial gas streams.[5] In addition, biochemists have long used CO as a probe ligand for the elucidation of structural and dynamic properties of reduced Cu-containing proteins and enzymes,[6] including hemocyanin[7] and cytochrome *c* oxidase.[8]

Historically, the first evidence for Cu(I) carbonyls was the observation by Leblanc[9] and Berthelot[10] that acidic solutions of Cu(I) salts absorbed up to 1 equiv of CO (based on Cu). The solid compound Cu(CO)Cl was first prepared by Wagner, who treated solid CuCl with 100 atm of CO.[11] Crystalline Cu(CO)Cl was subsequently isolated from solutions or suspensions of CuCl under 1 atm of CO.[12] Other simple Cu(CO)X salts have been reported for $X^- = CF_3CO_2^-$,[13] $C_2H_5SO_3^-$,[14] $CF_3SO_3^-$,[14] *t*-BuO$^-$,[15] and AsF_6^-.[16] In addition, many Cu(I) carbonyl complexes with amine ligands are known.[17] With one exception, the CO/Cu stoichiometric ratio in all known Cu(I) carbonyl compounds is ≤ 1.0. The exception is a report that solutions of Cu_2O in neat HSO_3F, $BF_3\cdot H_2O$, and other strong acids absorbed up to 4 equiv of CO/equiv of Cu, the exact stoichiometry being dependent on temperature and pressure.[18] On the basis of this report, IR[18] and Raman[19] spectra of these solutions were interpreted in terms of the following set of equilibria:

$$\mathrm{Cu^+(solv)} \underset{-\mathrm{CO}}{\overset{+\mathrm{CO}}{\rightleftharpoons}} [\mathrm{Cu(CO)}]^+\mathrm{(solv)} \underset{-2\mathrm{CO}}{\overset{+2\mathrm{CO}}{\rightleftharpoons}} [\mathrm{Cu(CO)_3}]^+\mathrm{(solv)} \underset{-\mathrm{CO}}{\overset{+\mathrm{CO}}{\rightleftharpoons}} [\mathrm{Cu(CO)_4}]^+\mathrm{(solv)}$$

None of these carbonyl complexes could be isolated as solids. For reasons that are not clear, other possible interpretations of the data, especially the existence of the dicarbonyl complex $[Cu(CO)_2]^+$, were not considered.

Prompted by this exception[18,19] and by the growing interest in nonclassical (predominantly σ-bonded) carbonyls of the coinage metals,[20] we are reinvestigating literature reports of Cu(I) carbonyls of the type Cu(CO)X. In this paper, we report that solid $CuAsF_6$ absorbs up to 3 equiv of CO *in the solid state* at $\leq$ 1 atm of CO. Vibrational spectra of neat samples recorded under precise pressures of CO indicate the existence of $[Cu(CO)][AsF_6]$, $[Cu(CO)_2][AsF_6]$, and $[Cu(CO)_3][AsF_6]$, all of which are very different in appearance. This suggests that

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(2) (a) Solomon, E. I.; Jones, P. M.; May, J. A. *Chem. Rev.* **1993**, *93*, 2623. (b) Waugh, K. C. *Catal. Today* **1992**, *15*, 51. (c) Bridger, G. W.; Spencer, M. S. In *Catalysis Handbook*, 2nd ed.; Twigg, M. V., Ed.; Wolfe Publishing Ltd.: London, 1989; p 441. (d) Henrici-Olivé, G.; Olivé, S. *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*; Springer-Verlag: Berlin, 1984; p 131. (e) Herman, R. G. In *New Trends in CO Activation*; Guczi, L., Ed.; Studies in Surface Science and Catalysis 64; Elsevier: Amsterdam, 1991; p 265.

(3) Lloyd, L.; Ridler, D. E.; Twigg, M. V. In *Catalysis Handbook*, 2nd ed.; Twigg, M. V., Ed.; Wolfe Pub. Ltd.: London, 1989; p 283.

(4) (a) Kawasaki, H.; Nakamoto, Y.; Yamamoto, A.; Kato, T.; Yamada, T. *Sekiyu Gakkaishi* **1994**, *37*, 529. (b) Souma, Y. *Shokubai Gakkai* **1987**, *29*, 317. (c) Souma, Y. *Osaka Kogyo Gijutsu Shikensho Hokoku* **1979**, 1. (d) Souma, Y.; Sano, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3296. (f) Bregault, J. M.; Jarjour, C.; Yolou, S. *J. Mol. Catal.* **1978**, *4*, 225. (g) Tsuda, T.; Isegawa, Y.; Saegusa, T. *J. Org. Chem.* **1972**, *37*, 2670.

(5) (a) Peng, X. D.; Golden, T. C.; Pearlstein, R. M.; Pierantozzi, R. *Langmuir* **1995**, *11*, 534 and references therein. (b) Kumar, R.; Kratz, W. C.; Guro, D. E.; Golden, T. C. *Process Technol. Proc.* **1994**, *11*, 383. (c) Su, C.; Che, Y.; Duannu, Q.; Wang, Y. *Huanjing Kexue* **1994**, *15*, 38. (d) Gholap, R. V.; Chaudhari, R. V. *Can. J. Chem. Eng.* **1992**, *70*, 505. (e) Koschel, J.; Pfennig, A.; Henschke, M.; Hartmann, H. *Energy Fuels* **1991**, *5*, 729.

(6) (a) Caulton, K. G.; Davies, G.; Holt, E. M. *Polyhedron* **1990**, *9*, 2319. (b) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Congr. Naz. Chim. Inorg.* **1979**, *12*, 50.

(7) (a) Hazes, B.; Magnus, K. A.; Bonaventura, C.; Bonaventura, J.; Dauter, Z.; Kalk, K. H.; Hol, W. G. *J. Protein Sci.* **1993**, *2*, 597, and references therein. (b) Blackburn, N. J.; Strange, R. W.; Reedijk, J.; Volbeda, A.; Farooq, A.; Karlin, K. D.; Zubieta, J. *Inorg. Chem.* **1989**, *28*, 1349, and references therein. (c) Solomon, E. I. In *Copper Proteins*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1981; p 41. (d) Vanneste, M.; Mason, H. S. In *The Biochemistry of Copper*; Peisach, J.; Aisen, P.; Blumberg, W. E., Eds.; Academic Press: New York, 1966; p 465.

(8) (a) Dyer, R. B.; Peterson, K. A.; Stoutland, P. O.; Woodruff, W. H. *Biochemistry* **1994**, *33*, 500. (b) Hill, B. C. *FEBS Lett.* **1994**, *354*, 284. (c) Hosler, J. P.; Kim, Y.; Shapleigh, J.; Gennis, R.; Alben, J.; Ferguson-Miller, S.; Babcock, G. *J. Am. Chem. Soc.* **1994**, *116*, 5515.

(9) Leblanc, F. *C. R. Acad. Sci. Paris* **1850**, *30*, 483.

(10) Berthelot, M. *Ann. Chim. Phys.* **1856**, *346*, 477.

(11) Wagner, O. H. *Z. Anorg. Chem.* **1931**, *196*, 364.

(12) (a) Håkansson, M.; Jagner, S. *Inorg. Chem.* **1990**, *29*, 5241. (b) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. A. *Inorg. Chem.* **1981**, *20*, 3382. (c) Backen, W.; Vestin, R. *Acta Chem. Scand.* **1979**, *A33*, 85.

(13) Scott, A. F.; Wilkening, L. L.; Rubin, B. *Inorg. Chem.* **1969**, *8*, 2533.

(14) Doyle, G.; Eriksen, K. A.; Van Engen, D. *Inorg. Chem.* **1983**, *22*, 2892.

(15) Tsuda, T.; Habu, H.; Horiguchi, S.; Saegusa, T. *J. Am. Chem. Soc.* **1974**, *96*, 5930.

(16) Desjardins, C. D.; Edwards, D. B.; Passmore, J. *Can. J. Chem.* **1979**, *57*, 2714.

(17) (a) Karlin, K. D.; Tyeklár, Z.; Farooq, A.; Haka, M. S.; Ghosh, P.; Cruse, R. W.; Gultneh, Y.; Hayes, J. C.; Toscano, P. J.; Zubieta, J. *Inorg. Chem.* **1992**, *32*, 1436. (b) Ardizzoia, G. A.; Beccalli, E. M.; La Monica, G.; Masciocchi, N.; Moret, M. *Inorg. Chem.* **1992**, *31*, 2706, and references therein. (c) Villacorta, G. M.; Lippard, S. J. *Inorg. Chem.* **1987**, *26*, 3672. (d) Pasquali, M.; Floriani, C. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, NY, 1983; p 311. (e) Bruce, M. I. *J. Organomet. Chem.* **1972**, *44*, 209.

(18) Souma, Y.; Iyoda, J.; Sano, H. *Inorg. Chem.* **1976**, *15*, 968.

(19) Neppel, A.; Hickey, J. P.; Butler, I. S. *J. Raman Spectrosc.* **1979**, *8*, 57.

(20) (a) Meyer, F.; Chen. Y.-M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 4071. (b) Schröder, D.; Hrušák, J.; Hertwig, R. H.; Koch, W.; Schwerdtfeger, P.; Schwarz, H. *Organometallics* **1995**, *14*, 423. (c) Hurlburt, P. K.; Rack, J. J.; Luck, J. S.; Dec, S. F.; Webb, J. D., Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 10003. (d) Aubke, F.; Wang, C. *Coord. Chem. Rev.* **1994**, *137*, 483. (e) Veldkamp, A.; Frenking, G. *Organometallics* **1993**, *12*, 4613. (f) Willner, H.; Schaebs, J.; Hwang, G.; Mistry, F.; Jones, R.; Trotter, J.; Aubke, F. *J. Am. Chem. Soc.* **1992**, *114*, 8972. (g) Adelhelm, M.; Bacher, W.; Höhn, E. G.; Jacob, E. *Chem. Ber.* **1991**, *124*, 1559. (h) Calderazzo, F. *J. Organomet. Chem.* **1990**, *400*, 303. (i) Barnes, L. A.; Rosi, M.; Bauschlicher, C. W. *J. Chem. Phys.* **1990**, *93*, 609.

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polycarbonyls of Cu(I) should be considered potential intermediates for heterogeneous Cu-containing catalysts in the presence of CO. It also suggests that solid-phase gas purification systems with capacities far exceeding current systems based on CuCl are possible.

We prepared $CuAsF_6$ according to a literature procedure.[21,22] The off-white solid is extremely moisture-sensitive. When it was exposed to CO at 23 °C, some of the gas was absorbed by the solid. For a typical experiment, the stoichiometries, based on moles absorbed CO per mole of Cu, were as follows: $CO/Cu = 0.47$ at 3 Torr; $CO/Cu = 1.6$ at 10 Torr; $CO/Cu = 2.6$ at 239 Torr. At pressures from 239 to 541 Torr, the CO/Cu mole ratio remained constant at ~2.6. The highest CO/Cu mole ratio observed at 541 Torr for any sample was 2.9. X-ray powder diffraction data for samples of $CuAsF_6$ matched the literature report,[21] indicating that no significant amount of another crystalline phase was present. Nevertheless, small amounts of impurities may be present in even the most carefully handled samples of $CuAsF_6$: Desjardins and Passmore[21] noted that $CuAsF_6$ contained several percent of a paramagnetic impurity, possible Cu(II), but it was still white in appearance. If we assume that the samples of $CuAsF_6$ contained ~90% of the stoichiometric amount of anhydrous Cu(I) ions, then the corrected CO/Cu(I) ratios at 3, 10, and 239 Torr were 0.52, 1.8, and 2.9, respectively. These values are consistent with the vibrational spectra discussed below. Furthermore, even though precise values of CO/Cu(I) are not known at this time for a particular pressure, it is clear that a significant amount of the *tricarbonyl* $[Cu(CO)_3][AsF_6]$ is formed at pressures well below 1 atm.

The appearance of samples of $[Cu(CO)_n][AsF_6]$ changed dramatically during the gas titrations: at 0 Torr CO, the solid sample was off-white; at 3 Torr, both off-white and very dark brown solids were present; at pressures slightly greater than 3 Torr, less off-white solid and more dark brown solid were present; at 10 Torr, the sample was almost entirely a colorless, low-melting, glassy solid with a small amount of dark solid present; at pressures greater than 100 Torr, the sample was entirely a bright white solid which did not change in appearance up to 541 Torr, the highest pressure used. The binding of CO to $CuAsF_6$ is reversible. At the end of the titrations, when CO was removed under vacuum, the bright white solid quickly (minutes) became a colorless glassy solid. After several hours under vacuum, the sample had become a dark solid. The titration data, taken together with the changes in appearance of the samples during the titrations, indicate that at 3 Torr we have a mixture of $CuAsF_6$ (off-white) and $[Cu(CO)][AsF_6]$ (dark brown), at 10 Torr mostly $[Cu(CO)_2][AsF_6]$ (colorless, glassy solid) plus some $[Cu(CO)][AsF_6]$, and at 239 Torr exclusively $[Cu(CO)_3][AsF_6]$ (bright white).

IR and Raman spectra (Supporting Information) are entirely consistent with these conclusions. The IR value of $\nu(CO)$ for $[Cu(CO)][AsF_6]$ (3 Torr of CO) is 2178 cm^{-1} (lit.[16] 2180 ± 5 cm^{-1}). For comparison, $\nu(CO)$ values for Cu(CO)Cl,[23] $[Cu(CO)][CF_3CO_2]$,[13] $[Cu(CO)][C_2H_5SO_3]$,[14] $[Cu(CO)][CF_3SO_3]$,[14] and $[Cu(CO)][t\text{-BuO}]$[15] are 2127, 2155, 2117, 2128, and 2062 cm^{-1}, respectively. Due to an extremely large fluorescence background, we were not able to obtain a Raman spectrum of $[Cu(CO)][AsF_6]$. The mutually exclusive IR and Raman $\nu(CO)$ bands at 2164 (Σ_u^+) and 2177 (Σ_g^+) cm^{-1}, respectively, for the glassy solid $[Cu(CO)_2][AsF_6]$ (10 Torr of CO) strongly suggest a linear $D_{\infty h}$ symmetry for the $[Cu(CO)_2]^+$ ion. Note that the analogous d^{10} ions $[Ag(CO)_2]^+$,[20c] $[Au(CO)_2]^+$,[20f] and $[Hg(CO)_2]^{2+}$ [24] also have $D_{\infty h}$ symmetry. The IR and Raman spectra for the bright white solid $[Cu(CO)_3][AsF_6]$ (200 Torr of CO; see illustrated synopsis on Table of Contents) are consistent with a trigonal planar D_{3h} symmetry for the $[Cu(CO)_3]^+$ ion: the band at 2183 cm^{-1} in the IR and at 2179 cm^{-1} in the Raman, which are the same within experimental error, are assigned to the E′ mode, and the band at 2206 cm^{-1} is assigned to the A_1' mode. The E′ mode for D_{3h} $[Ag(CO)_3]^+$ was found at 2192 cm^{-1}.[25]

A few compounds with a CO ligand bridging two Cu(I) ions have been reported. Typical $\nu(CO)$ values for the bridging CO ligands are 1900−1960 cm^{-1}.[26] On the basis of the very high $\nu(CO)$ values observed for $[Cu(CO)_n][AsF_6]$, we do not believe that any of the species formed in our experiments contain bridging carbonyl ligands.

Armentrout and co-workers have just reported metal-carbonyl bond energies of the gas phase complex ions $[Cu(CO)_n]^+$ and $[Ag(CO)_n]^+$ ($n = 1-4$):[20a] $(CO)_xCu^+{-}CO$ bond energies at 0 K are 36(2), 41(1), 18(1), and 13(1) kcal mol^{-1} for $x = 0, 1, 2$, and 3, respectively; $(CO)_xAg^+{-}CO$ bond energies at 0 K are 21(1), 26(1), 13(2), and 11(4) kcal mol^{-1} for $x = 0, 1, 2$, and 3, respectively (the values for Ag(I) are in excellent agreement with recent theoretical predictions of Veldkamp and Frenking[20e]). Our results are in harmony with these measurements in that $CuAsF_6$ forms a tricarbonyl complex at less than 1 atm of CO while $AgSbF_6$ does not form even a monocarbonyl complex of Ag(I) at 1 atm of CO.[20c] While this may at first seem counterintuitive because the first gas-phase Ag(I)−CO bond energy is slightly larger than the third gas-phase Cu(I)−CO bond energy, $[Cu(CO)_2][AsF_6]$ has already been "promoted" in that Cu(I)···F contacts in $[Cu(CO)_2][AsF_6]$ are undoubtedly fewer in number and weaker in energy than in $CuAsF_6$ or in $AgSbF_6$.

Our results suggest that other copper(I) salts of weakly coordinating anions may have higher affinities for more than one CO ligand than previously believed. Our results also suggest that the uptake of CO by acidic solutions of Cu(I)[18] and the vibrational spectra of these solutions[18,19] should be reinterpreted to include the likely presence of $[Cu(CO)_2]^+$ ions.

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Supporting Information Available: Figure 1, showing IR and Raman spectra of neat samples of $CuAsF_6$ plus varying pressures of CO (1 page). Ordering information is given on any current masthead page.

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(21) Desjardins, C. D.; Passmore, J. *J. Fluorine Chem.* **1975**, *6*, 379.

(22) ^{19}F NMR (SO_2ClF): δ −6.87. IR: 685 cm^{-1} (T_{1u} ν(As−F)). Raman: 682 cm^{-1} (A_{1g} ν(As−F). The E_g ν(As−F) was not observed in the Raman spectrum due to an inadequate signal/noise ratio.

(23) Håkansson, M.; Jagner, S.; Kettle, S. F. A. *Spectrochim. Acta* **1992**, *48A*, 1149.

(24) Willner, H.; Bodenbinder, M.; Wang, C.; Aubke, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1189.

(25) Rack, J. J.; Moasser, B.; Gargulak, J. D.; Gladfelter, W. L.; Hochheimer, H. D.; Strauss, S. H. *J. Chem. Soc., Chem. Commun.* **1994**, 685.

(26) (a) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Guastini, C. *J. Am. Chem. Soc.* **1981**, *103*, 185. (b) Pasquali, M.; Floriani, C.; Venturi, G.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1981**, *103*, 185. (c) Doyle, G.; Eriksen, K. A.; Modrick, M.; Ansell, G. *Organometallics* **1982**, *1*, 1613.