Inorg. Chem. **2000,** *39,* 1735−1742

Weakly Coordinating Anions HA_2^- Generated from Oxoanions A^- and Their Conjugate Acids. Coordination Equilibria, Ionic Conductivities, and the Structures of $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$ and $[Cu(CO)(H(CF_3CO_2)_2)]_2$

Oleg G. Polyakov, Benjamin G. Nolan, Benjamin P. Fauber, Susie M. Miller, Oren P. Anderson, and Steven H. Strauss*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received October 4, 1999

The coordination or ion pairing of the hydrogen-bonded anions $H(CF_3CO_2)_2^-$ and $H(CH_3SO_3)_2^-$ to NEt_4^+, Li^+, Cu^+, and/or Cu^{2+} was investigated. The structure of $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$ consists of centrosymmetric dimeric moieties that contain two homoconjugated $(CH_3SO_2O-H\cdots OSO_2CH_3)^-$ anions per Cu^{2+} ion, forming typical Jahn−Teller tetragonally elongated CuO_6 coordination spheres. The oxygen atoms involved in the nearly linear $O-H\cdots O$ hydrogen bonds ($O\cdots O \sim 2.62$ Å) are not coordinated to the Cu^{2+} ions. The structure of $Cu_2(CO)_2(H(CF_3CO_2)_2)_2$ consists of pseudo-C_2-symmetric dimers that contain one homoconjugated $(CF_3COO-H\cdots OCOCF_3)^-$ anion per Cu^+ ion, forming highly distorted tetrahedral $Cu(CO)O_3$ coordination spheres. Three of the four oxygen atoms in each hydrogen-bonded $H(CF_3CO_2)_2^-$ anion are coordinated to the Cu^+ ions, including one of the oxygen atoms in each $O-H\cdots O$ hydrogen bond ($O\cdots O \sim 2.62$ Å). Infrared spectra (ν(CO) values) of $Cu(CO)(CF_3CO_2)$ or $Cu(CO)(CH_3SO_3)$ dissolved in acetonitrile or benzene, with and without added CF_3COOH or CH_3SO_3H, respectively, demonstrate that HA_2^- anions involving carboxylates or sulfonates are more weakly coordinating than the parent anions RCO_2^- and RSO_3^-. Direct current conductivities of THF solutions of $Li(CF_3CO_2)$ containing varying concentrations of added CF_3COOH further demonstrate that Li^+ and NEt_4^+ ion pair much more weakly with $H(CF_3CO_2)_2^-$ than with $CF_3CO_2^-$.

Introduction

Weakly coordinating anions[1] such as BF_4^-, PF_6^-, $SbCl_6^-$, $AlCl_4^-$, $Al(OC(Ph)(CF_3)_2)_4^-$,[2] $Sb(OTeF_5)_6^-$,[3] $Co(C_2B_9H_{11})^-$,[4] and $Ag(CB_{11}H_6Br_6)_2^-$ [5] can be thought of as complexes of a central cation and a suitable number of identical anionic fragments (this is conceptually useful even though some of the cations, such as B^{3+}, do not have an independent existence). One member of this class consists of oxoanions A^- hydrogen-bonded to their conjugate acids HA to form HA_2^- anions.[6] Although the simplest example, $H(OH)_2^-$, might be expected to be rather strongly coordinating, anions such as $H(RCO_2)_2^-$ should be weakly coordinating because of the decrease in negative charge density on the oxygen atoms relative to the parent RCO_2^- anion. Gas-phase dissociation enthalpies for the strongest $O-H\cdots O$ hydrogen bonds are ca. 30 kcal/mol (e.g., $H(CH_3CO_2)_2^-$, 29.3 kcal/mol).[7] Although this is considerably lower than the gas-phase enthalpies of F^- dissociation from BF_4^- (92(6) kcal mol^{-1}),[8] PF_6^- (101(8) kcal mol^{-1}),[9] and even HF_2^- (39(1) kcal mol^{-1}),[10] the fragmentation of a particular HA_2^- anion into HA and A^- may be sufficiently endothermic to afford stable complexes in some cases.

Structurally characterized examples of simple HA_2^- oxoanions include $H(OH)_2^-$ (mixed Na^+/$NMeEt_3^+$ salt),[11] $H(SO_3F)_2^-$ (Cs^+ salt),[12] $H(NO_3)_2^-$ (Cs^+ salt),[13] $H(CH_3CO_2)_2^-$ (K^+ salt),[14] $H(CF_3CO_2)_2^-$ (K^+ salt),[15] and $H(OTeF_5)_2^-$ ($N(n\text{-}Bu)_4^+$ salt).[16] In this paper we present spectroscopic, conductometric, and structural data that examine the coordinating and ion-pairing properties of the $H(CF_3CO_2)_2^-$ and $H(CH_3SO_3)_2^-$ anions relative to the parent oxoanions $CF_3CO_2^-$ and $CH_3SO_3^-$. There are many examples of transition-metal complexes containing the $H(OH)_2^-$ anion.[17] However, when this work was started there was only

---

(1) (a) Lupinetti, A. J.; Strauss, S. H. *Chemtracts—Inorg. Chem.* **1998**, *11*, 565. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

(2) Barbarich, T. J.; Handy, S. T.; Miller, S. M.; Anderson, O. P.; Grieco, P. A.; Strauss, S. H. *Organometallics* **1996**, *15*, 3776.

(3) (a) Mercier, H. P. A.; Sanders, J. C. P.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 2921. (b) Van Seggen, D. M.; Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 3453.

(4) Hawthorne, M. F.; Andrews, T. D.; Garrett, P. M.; Olsen, F. P.; Reintjes, M.; Tebbe, F. N.; Warren, S. F.; Wegner, P. A.; Young, D. C. *Inorg. Synth.* **1967**, *10*, 91.

(5) Xie, Z.; Bau, R.; Reed, C. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2433.

(6) (a) Speakman, J. C. *Struct. Bonding* **1972**, *12*, 141. (b) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91.

(7) (a) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7139. (b) Caldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4660. (c) Moet-Ner, M.; Sieck, L. W. *J. Am. Chem. Soc.* **1986**, *108*, 7525.

(8) Mallouk, T. E.; Rosenthal, G. L.; Müller, G.; Brusasco, R.; Bartlett, N. *Inorg. Chem.* **1984**, *23*, 3167.

(9) Bartlett, N.; Okino, F.; Mallouk, T. E.; Hagiwara, R.; Lerner, M.; Rosenthal, G. L.; Kourtakis, K. *Adv. Chem. Ser.* **1990**, *226*, 391.

(10) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 5848.

(11) Abu-Dari, K.; Raymond, K. N.; Freyberg, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 3688.

(12) Belin, C.; Charbonnel, M.; Potier, J. *J. Chem. Soc., Chem. Commun.* **1981**, 1036.

(13) Roziere, J.; Roziere-Bories, M.-T.; Williams, J. T. *Inorg. Chem.* **1976**, *15*, 2490.

(14) Currie, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 832.

(15) Macdonald, A. L.; Speakman, J. C.; Hadži, D. *J. Chem. Soc., Perkin Trans. 2* **1972**, 825.

(16) Strauss, S. H.; Abney, K. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 2806.

(17) (a) Ardon, M.; Bino, A. *Struct. Bonding* **1987**, *65*, 1. (b) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875. (c) Schneider, R.; Weyhermuller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1993**, *32*, 4925.

10.1021/ic991165f CCC: $19.00

one structurally characterized transition-metal complex containing a homoconjugated HA_2^- oxoanion ligand, $[CpFe(CO)_2]_2[H(Me_2C{=}CHCO_2)_2]$.[18] Two examples of structurally characterized complexes containing HF_2^- ligands are $Mo(H)_2(PMe_3)_4F(HF_2)$ and *trans*-$RuH(dmpe)_2(HF_2)$.[19]

Experimental Section

Materials and Reagents. Many of the compounds studied were sensitive to oxygen and/or water. Accordingly, preparations and physical measurements were carried out with rigorous exclusion of air and water. Carbon monoxide (Matheson) was passed through columns containing activated BASF R3 catalyst and activated 4 Å molecular sieves. The compounds Cu_2O (Aldrich) and anhydrous CF_3CO_2H (Aldrich) were used as received. To prove that the acid was sufficiently dry, ^1H NMR spectra of the acid dissolved in dry acetonitrile-d_3, with and without added $(CF_3CO)_2O$, were obtained. The δ value for the acidic H atom was the same in both cases; control experiments demonstrated that traces of water cause a shift in δ. Methylsulfonic acid, CH_3SO_3H (Aldrich), was dried with activated 4 Å molecular sieves, filtered, and stored under nitrogen. The salts $LiCF_3CO_2$ (Aldrich) and $NEt_4(CF_3CO_2)$ (Aldrich) were dried by heating under vacuum for 18 h at 110 or 35 °C, respectively. The following solvents were distilled under a nitrogen atmosphere from the indicated drying agents: benzene (Na); THF (Na); acetonitrile (CaH_2). The compounds $Cu(CO)(CH_3SO_3)$ and $Cu(CO)(CF_3CO_2)$ were prepared by literature procedures.[20]

$\{Cu_2(H(CH_3SO_3)_2)_4\}_n$. The compound Cu_2O (1 g) was mixed with 5 mL of anhydrous CH_3SO_3H under a dry dioxygen atmosphere. After several weeks, off-white crystals suitable for diffraction had formed. These were separated from the bulk of the solids present by decantation. The crystals could not be dried under vacuum without causing decomposition of the compound via loss of CH_3SO_3H from the $H(CH_3SO_3)_2^-$ ion in the solid state. For this reason, a meaningful % yield and a meaningful elemental analysis could not be obtained.

$[Cu(CO)(H(CF_3CO_2)_2)]_2$. The compounds $Cu(CO)(CF_3CO_2)$ and CF_3COOH were mixed in dichloromethane under a CO atmosphere in a 1:5 molar ratio. Cooling the resulting colorless solution to −5 °C resulted in the formation of white crystals suitable for diffraction. As above, the crystals could not be dried under vacuum without causing decomposition of the compound via loss of CF_3COOH from the $H(CF_3CO_2)_2^-$ ion in the solid state. For this reason, a meaningful % yield and a meaningful elemental analysis could not be obtained.

$LiCB_{11}H_{12}$. The compound $[NHMe_3][CB_{11}H_{12}]$[21] (0.998 g, 4.92 mmol) was dissolved in dry THF (25 mL) and was treated with *n*-BuLi (4.92 mmol; dropwise; 25 °C). The cloudy mixture was stirred for 1 h. At this point, all volatiles (THF and NMe_3) were removed under vacuum to leave a white solid, which was dried under vacuum (10^{-3} Torr) at 210 °C for 6 h to yield 0.590 g of $LiCB_{11}H_{12}$ as a white powder (80% yield). $^{11}B\{^1H\}$ NMR (CD_3CN): δ −5.84 (intensity 1), −12.31 (intensity 5), −15.38 (intensity 5).

Physical Methods. IR Spectroscopy. Samples for IR spectroscopy were either Fluorolube mulls between AgCl windows or solutions in a ~0.5 mm gastight Teflon cell of local design. Spectra were recorded on a Nicolet 5PC FTIR spectrometer operating at 2 cm^{-1} resolution. The crystalline samples contained traces of excess CH_3SO_3H or CF_3COOH. For this reason, the $\nu(OH)$, $\nu(SO)$, and $\nu(CO)$ regions of the spectra will not be discussed.

Table 1. Crystallographic Data for $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$ and $[Cu(CO)(H(CF_3CO_2)_2)]_2$

	$\{Cu_2(H(CH_3SO_3)_2)_4\}_n$	$[Cu(CO)(H(CF_3CO_2)_2)]_2$
chemical formula	$C_4H_{14}CuO_{12}S_4$	$C_{10}H_2Cu_2F_{12}O_{10}$
fw, g mol^{-1}	445.93	637.20
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
unit cell dimens		
a, Å	8.4533(9)	8.351(2)
b, Å	8.489(2)	10.129(6)
c, Å	10.1247(8)	12.331(6)
α, deg	90.29(2)	83.70(5)
β, deg	91.582(7)	73.47(3)
γ, deg	102.35(1)	88.43(5)
V, $Å^3$	709.4(2)	993.8(8)
Z	2	
T, °C	−100(1)	−110(1)
λ, Å	0.71073	0.71073
abs coeff, cm^{-1}	21.86	22.98
$R(F_o^2)$ $(I > 2\sigma(I))$	0.063	0.048
$R_w(F_o^2)$ (all data)	0.190	0.134

DC Conductometry. Solution conductivities were measured at 25 °C in a nitrogen-filled glovebox using a Yellow Springs Instrument (YSI) model 31A conductance bridge and a YSI model 3403 cell that was calibrated for inverted use (cell constant $k = 1.11$ cm^{-1}). Solutions were prepared in the glovebox by adding THF to weighed samples in 5 mL volumetric flasks. The conductivity of the THF used was determined to be less than or equal to 3×10^{-7} S cm^{-1}, the lowest conductivity measurable with this apparatus.

Single-Crystal X-ray Diffraction Studies. For $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$, X-ray diffraction data from a crystal of dimensions 0.3 × 0.3 × 0.2 mm were recorded on a Bruker P4 diffractometer employing Mo Kα radiation (graphite monochromator). Crystallographic results and other details are listed in Table 1. The cell parameters were obtained from a least-squares fit to the angular coordinates of 25 reflections. Intensities were obtained by standard $\theta-2\theta$ scans. An empirical absorption correction was applied by using the results from ψ scans on selected reflections. The structure was solved by direct methods and refined (on F^2, using all data) by a full-matrix, weighted least-squares process. All non-hydrogen atoms were refined by using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined by using a riding model with the exception of those attached to O2 and O9. Both were refined, holding the O−H bond length at a constrained distance with a constraint tightness of 0.01 Å on an idealized constraint distance of 1.00 Å. The final electron density map showed features in the range −2.13 to +1.44 e $Å^{-3}$, with the highest peak being 1.08 Å from S2. Bruker SHELXTL[22] software was used for structure solution, refinement, and graphics.

For $[Cu(CO)(H(CF_3CO_2)_2)]_2$, X-ray diffraction data were recorded on a Bruker SMART CCD diffractometer employing Mo Kα radiation (graphite monochromator). Crystallographic results and other details are listed in Table 1. The cell parameters were obtained from a least-squares fit to the angular coordinates of 151 reflections on a series of oscillation frames. Intensities were integrated from a series of frames (0.3° ω rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied by using SADABS.[23] The structure was solved by direct methods and refined (on F^2, using all data) by a full-matrix, weighted least-squares process. All non-hydrogen atoms were refined by using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined by using a riding model with the exception of those attached to O4 and O6. Both were refined, holding the O−H bond length at a constrained distance with a constraint tightness of 0.01 Å on an idealized constraint distance of 1.00 Å. Disorder involving the trifluoromethyl group centered on C4 was modeled by including two fractional sets of fluorine atoms, each constrained to idealized geometry. The

---

(18) (a) $[CpFe(CO)_2]_2[H(Me_2C{=}CHCO_2)_2]$: Cupertino, d. C.; Harding, M. M.; Cole-Hamilton, D. J.; Dawes, H. M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 1129. (b) Although it has not been structurally characterized, the compound $[Cp^*{}_2SiH][H_3(cat)_2]$ appears to contain the homoconjugated hydrogenbis(hydrogen-catecholate) monoanion: Jutzi, P.; Bunte, E.-A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1605.

(19) (a) $Mo(H)_2(PMe_3)_4F(HF_2)$: Murphy, V. J.; Hascall, T.; Chen. J. Y.; Parkin, G. *J. Am. Chem. Soc.* **1996**, *118*, 7428. (b) *trans*-$RuH(dmpe)_2(HF_2)$: Whittlesey, M. K.; Perutz, R. N.; Greener, B.; Moore, M. H. *Chem. Commun.* **1997**, 187.

(20) (a) Doyle, G.; Eriksen, K. A.; van Engen, D. *Inorg. Chem.* **1983**, *22*, 2892. (b) Scott, A. F.; Wilkening, L. L.; Rubin, B. *Inorg. Chem.* **1969**, *8*, 2533.

(21) Plešek, J.; Jelínek, T.; Drdáková, E.; Heřmánek, S.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1559.

(22) Sheldrick, G. M. *SHELXTL*, v. 5.03; Bruker AXS: Madison, WI, 1995.

(23) Sheldrick, G. M. *SADABS—a program for area detector absorption corrections.*

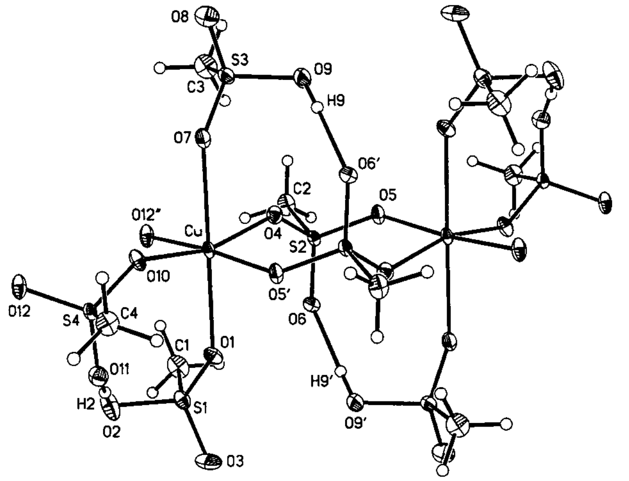


Figure 1. Structure of $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$, showing a centrosymmetric dimeric piece (two symmetry-related Cu^{2+} ions) of the polymer (50% probability ellipsoids except for H atoms, which are shown as circles of arbitary size). Note the Jahn−Teller-distorted octahedral environment of the Cu^{2+} ion (Cu−O1, 2.324(5); Cu−O4′, 2.016(5) Å; Cu−O5, 1.955(5) Å; Cu−O7, 2.366(5) Å; Cu−O10, 2.001(5) Å; Cu−O12″, 1.969(5) Å). The two O−H···O hydrogen bonds are O2−H2···O11 (O2···O11, 2.604(8) Å; O2−H2, 0.85 Å; H2···O11, 1.76 Å; O2−H2−O11, 175°) and O9−H9−O6 (O9···O6, 2.621(8) Å; O9−H9, 0.85 Å; H9···O6, 1.78 Å; O9−H9···O6′, 179°).

final electron density map showed features in the range −0.62 to +1.35 e $Å^{-3}$. Bruker SHELXTL[22] software was used for structure solution, refinement, and graphics. Further details of the data collection and structure determination for both structures are listed in the Supporting Information.

Results and Discussion

There are two important questions concerning homoconjugated HA_2^- anions as ligands that were addressed in this work. First, is it possible to isolate binary transition-metal salts $M(HA_2)_m$, where m is an integer, which are related to the set of simpler binary transition-metal salts MA_m? Second, is an HA_2^- ligand more weakly coordinating than the corresponding A^- ligand? The first question has now been answered in the affirmative for the $H(CH_3SO_3)_2^-$ anion by the isolation and structural characterization of a Cu^{2+} salt of empirical formula $Cu(H(CH_3SO_3)_2)_2$. The second question has also been answered in the affirmative for $H(CH_3SO_3)_2^-$ vs $CH_3SO_3^-$ and for $H(CF_3CO_2)_2^-$ vs $CF_3CO_2^-$ by studying ν(CO) values for Cu^+ derivatives and, in the case of $H(CF_3CO_2)_2^-$ vs $CF_3CO_2^-$, solution conductivities of $Li(CF_3CO_2)$ and $NEt_4(CF_3CO_2)$ with and without added CF_3COOH.

Structure of $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$. The structure of this copper(II) compound, shown in Figure 1, consists of centrosymmetric dimeric moieties that contain two $[CH_3SO_2O-H\cdots OSO_2CH_3]^-$ anions per Cu^{2+} ion. Selected distances and angles are listed in Table 2. As far as we are aware, this is the only structurally characterized example of a "bisulfonate" $H(RSO_3)_2^-$ anion other than $H(FSO_3)_2^-$ [12] and is the only structurally characterized example of a homoleptic HA_2^- transition-metal compound. The oxygen atoms involved in the nearly linear O−H···O hydrogen bonds in $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$ are not coordinated to the Cu^{2+} ions. Three of the four remaining oxygen atoms of each HA_2^- anion are coordinated to the Cu^{2+} ions. Therefore, only one oxygen atom per anion (O3 in one anion and O8 in the other) is not associated with either of the two types of Lewis acids in the structure. Note also that the $[Cu_2(H(CH_3SO_3)_2)_4]$ dimers are not discrete molecules; they are linked together by Cu−O10 and Cu−O12″ bonds, forming a chain of dimers.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $\{[Cu_2(H(CH_3SO_3)_2)_4]\}_n$

Cu−O1	2.323(5)	Cu−O4	2.016(5)
Cu−O5′	1.955(5)	Cu−O7	2.366(5)
Cu−O10	2.000(5)	Cu−O1″	1.968(5)
S1−O1	1.447(5)	S1−O2	1.551(5)
S1−O3	1.422(5)	S2−O4	1.459(5)
S2−O5	1.476(5)	S2−O6	1.453(5)
S3−O7	1.433(5)	S3−O8	1.436(5)
S3−O9	1.559(5)	S4−O10	1.463(5)
S4−O11	1.450(5)	S4−O12	1.476(5)
O2···O11	2.604(8)	O9···O6′	2.621(8)
O2−H2	1.00 (fixed)	O9−H9	1.00 (fixed)
H2···O11	1.64	H9···O6′	1.63
O1−Cu−O7	179.1(2)	O1−Cu−O4	97.7(2)
O1−Cu−O5′	86.8(2)	O1−Cu−O10	97.9(2)
O1−Cu−O12″	87.2(2)	O4−Cu−O10	164.3(2)
O4−Cu−O5′	92.1(2)	O4−Cu−O7	83.2(2)
O4−Cu−O12″	87.3(2)	O5′−Cu−O12″	173.8(2)
O5′−Cu−O7	93.2(2)	O5′−Cu−O10	88.9(2)
O7−Cu−O10	81.2(2)	O7−Cu−O12″	92.9(2)
O10−Cu−O12″	93.3(2)	O2−H2···O11	161
O9−H9···O6′	177	S1−O2−H2	104
S3−O9−H9	111		

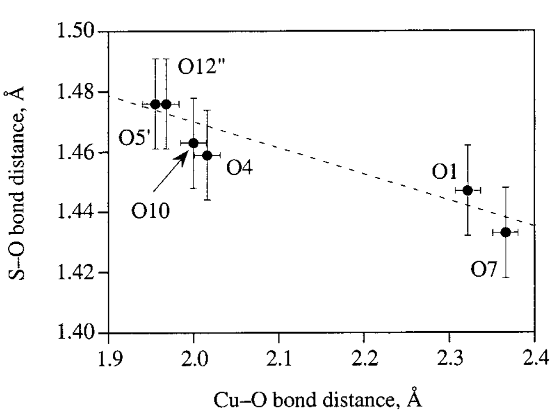


Figure 2. Plot of S−O vs Cu−O distances in the structure of $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$. The errors shown are $\pm 3\sigma$. Oxygen atoms O1 and O7 are weakly bonded to the Cu^{2+} ion (ca. 2.3 Å). The other four oxygen atoms are strongly bonded to the Cu^{2+} ion (ca. 2.0 Å). The dashed line is a visual aid only and has no special significance. Oxygen atoms O3 and O8 (not shown), which do not interact with the Cu^{2+} ion or with the two protons, exhibit S−O distances of ca. 1.43 Å.

The CuO_6 coordination sphere is tetragonally elongated, a Jahn−Teller distortion common for six-coordinate d^9 metal ions. The two long Cu−O1 and Cu−O7 bond distances are 2.323(5) and 2.366(5) Å, respectively, and the O1−Cu−O7 bond angle is 179.1(2)°. The four short Cu−O bonds range from 1.955(5) to 2.016(5) Å and form a nonplanar CuO_4 coordination unit with idealized D_{2d} symmetry. The Cu^{2+} ion in $\{[Cu_2(H(CH_3SO_3)_2)_4]\}_n$ is displaced 0.08 Å from the least-squares plane formed by the atoms O4, O5′, O10, O12″, each of which is displaced 0.19 Å from that plane. As might be expected, there is an inverse correlation between the Cu−O and S−O bond distances, as shown in Figure 2. For comparison, the axial $Cu-OSO_2CH_3$ bond distances in centrosymmetric $Cu(CH_3SO_3)_2(H_2O)_4$ are 2.387(2) Å[24] and the equatorial $Cu-OSO_2CH_3$ bond distances in centrosymmetric $\{Cu(CH_3SO_3)(C_4H_4N_2)_2\}_n$ are 1.956(1) Å[25] (these compounds also contain six-coordinate,

---

[24] Charbonnier, F.; Faure, R.; Loiseleur, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1845.

[25] Haynes, J. S.; Rettig, S. J.; Sams, J. R.; Thompson, R. C.; Trotter, J. *Can J. Chem.* **1987**, *65*, 420.

tetragonally elongated Cu^{2+} ions). The S−O(Cu) bond distances in these compounds are 1.441(2) and 1.483(1) Å, respectively, which fit the correlation shown in Figure 2.

Hydrogen bonding between two oxygen atoms was studied extensively in the 1960s and 1970s, especially after single-crystal X-ray and neutron diffraction techniques became widely available.[26,27] For O−H···O hydrogen bonds, there is a well-known inverse correlation between O−H distances determined by neutron diffraction, which range from ca. 1.25 to 0.95 Å, and O···O distances, which range from ca. 2.40 to 2.85 Å.[27] The O2···O11 and O6···O9′ interatomic distances in $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$ are 2.604(8) and 2.621(8) Å, respectively, significantly longer than the O···O distance of 2.41(1) Å in $CsH(FSO_3)_2$.[12] In the absence of a structure of an alkali metal salt or NR_4^+ salt of $H(CH_3SO_3)_2^-$, it is not possible to decide whether the difference in O···O distances is an intrinsic difference between the $H(CH_3SO_3)_2^-$ and $H(FSO_3)_2^-$ anions or is a consequence of the coordination of $H(CH_3SO_3)_2^-$ to Cu^{2+} ions.

Distances and angles involving H2 and H9 in $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$ must be considered as approximations only and are listed without estimated standard deviations, because the O2−H2 and O9−H9 distances were constrained to be 1.00 Å. This constraint is quite reasonable; neutron diffraction analyses have shown that O−H···O hydrogen bonds with O···O separations of ca. 2.6 Å have O−H bond distances of ca. 1.0 Å. Examples include (O···O and O−H distances, respectively, given in parentheses) $KH(HSeO_3)_2$ (2.602(2), 1.029(3) Å),[28] H_2SeO_3 (2.621(2), 1.009(3) Å),[29] and CH_3COOH (2.631(8), 1.011(15) Å).[30] With this caveat in mind, the O2−H2···O11 and O9−H9···O6′ hydrogen bonds in $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$ appear to be relatively undistorted as far as bond angles are concerned. The O2−H2···O11 and O9−H9···O6′ angles are 161° and 177°, respectively, and the S1−O2−H2 and S3−O9−H9 angles are 104° and 111°, respectively.

The hydroxyl hydrogen atoms were fixed relatively close to O2 and O9 because the S1−O2 and S3−O9 bonds, at 1.551(5) and 1.559(5) Å, are so much longer than the other S−O distances, which range from 1.436(5) to 1.476(5) Å. The observed asymmetry is probably due to the substantially greater basicity of the S1 and S3 methylsulfonates relative to the S2 and S4 methylsulfonates. Each S1 and S3 methylsulfonate makes only one Cu−O contact at ca. 2.3 Å, while each S2 and S4 anion makes two shorter and stronger Cu−O contacts at ca. 2.0 Å. In this regard, the S1 and S3 methylsulfonates, along with H2 and H9, can be considered as molecules of methylsulfonic acid that are (i) hydrogen bonded to other μ-κ^2-methylsulfonate ligands and (ii) weakly coordinated to the Cu^{2+} ion through the long Cu−O1 and Cu−O7 bonds. It is reasonable to propose that the generation of a (temporarily) vacant coordination site at the Cu^{2+} ion in $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$ might occur by a relatively low energy Cu−O7 bond-breaking process.

Structure of $[Cu(CO)(H(CF_3CO_2)_2)]_2$. The structure of this copper(I) compound, which is shown in Figure 3, consists of asymmetric dimeric molecules that contain one $CF_3COO{-}H\cdots OCOCF_3^-$ anion and one carbonyl ligand per Cu^+ ion. Selected interatomic distances and angles are listed in Table 3. Although there is no crystallographic symmetry, there is an idealized C_2 axis that passes through the eight-membered boat-shaped $\overline{\mathrm{Cu1{-}O7{-}C7{-}O8{-}Cu2{-}O10{-}C9{-}O9}}$ ring. In contrast to the structure of $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$, one of the oxygen atoms in each O−H···O hydrogen bond is also coordinated to a Cu^+ ion, a result that may be due to the $H(CF_3CO_2)_2^-$ anion having fewer donor atoms than the $H(CH_3SO_3)_2^-$ anion. Therefore, all of the oxygen atoms are bonded to Cu^+, H^+, or both types of Lewis acids.

The $Cu(CO)O_3$ coordination spheres can be described as severely distorted tetrahedra or as trigonal planes with very weak axial interactions; Cu1 is displaced 0.28 Å from the least-squares plane formed by C1, O7, and O9, and Cu2 is displaced 0.22 Å from the $\overline{\mathrm{C2{-}O8{-}O10}}$ least-squares plane. The Cu1−C1 distance and Cu1−C1−O1 angle are 1.817(7) Å and 176.3(6)°, respectively. The Cu1−O7 and Cu1−O9 distances are 2.074(4) and 2.035(4) Å, respectively, and the longer Cu1−O3

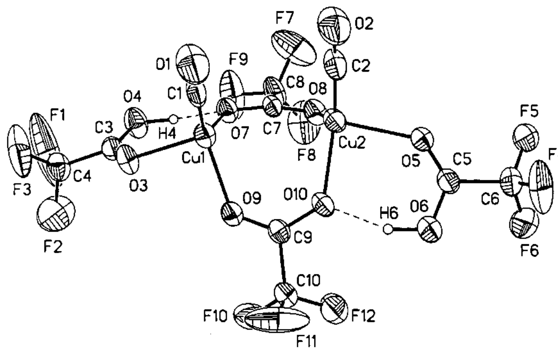


Figure 3. Structure of $[Cu(CO)(H(CF_3CO_2)_2)]_2$, a pseudo-$C_2$-symmetric dimer (50% probability ellipsoids except for the H atom, which is shown as a circle of arbitary size). Selected interatomic distances (Å) and angles (deg): Cu1−C1, 1.813(6); C1−O1, 1.128(7); Cu1−C1−O1, 176.6(5); Cu1−O3, 2.211(4); Cu1−O7, 2.074(4); Cu1−O9, 2.035(4); O4···O7, 2.636(7); C1−Cu1−O7, 127.7(2); C1−Cu1−O9, 126.0(2); O7−Cu1−O9, 99.8(1); Cu2−C2, 1.813(6); C2−O2, 1.129(7); Cu2−C2−O2, 176.9(6); Cu2−O5, 2.234(4); Cu2−O8, 2.017(4); Cu2−O10, 2.058(4); O6···O10, 2.622(7); C2−Cu2−O8, 126.6(2); C2−Cu2−O10, 130.4(2); O7−Cu1−O9, 98.9(1).

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $[Cu(CO)(H(CF_3CO_2)_2)]_2$

Cu1−C1	1.817(7)	C1−O1	1.123(7)
Cu1−O3	2.215(4)	Cu1−O7	2.074(4)
Cu1−O9	2.035(4)	Cu2−C2	1.816(7)
C2−O2	1.125(7)	Cu2−O5	2.232(4)
Cu2−O8	2.019(4)	Cu2−O10	2.059(4)
C3−O3	1.210(7)	C3−O4	1.287(7)
C5−O5	1.218(7)	C5−O6	1.285(7)
C7−O7	1.257(6)	C7−O8	1.241(6)
C9−O9	1.236(6)	C10−O10	1.259(6)
O4−H4	1.00 (fixed)	O6−H6	1.00 (fixed)
O7···H4	1.70	O10···H6	1.67
O4···O7	2.636(7)	O6···O10	2.622(7)
Cu1···Cu2	3.170(3)		
Cu1−C1−O1	176.3(6)	Cu2−C2−O2	177.5(6)
C1−Cu1−O3	113.6(2)	C1−Cu1−O7	127.5(2)
C1−Cu1−O9	126.2(2)	O3−Cu1−O7	86.5(2)
O3−Cu1−O9	90.6(2)	O7−Cu1−O9	99.8(2)
C2−Cu2−O5	107.8(2)	C2−Cu2−O8	126.4(2)
C2−Cu2−O10	130.5(2)	O5−Cu2−O8	92.4(2)
O5−Cu2−O10	86.5(2)	O8−Cu2−O10	98.9(2)
C3−O4−H4	111	C5−O6−H6	112
O4−H4···O7	155	O6−H6···O10	160

---

(26) (a) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; Benjamin: San Francisco, 1968. (b) Joeston, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker: New York, 1974. (c) Schuster, P., Zundel, G., Sandorfy, C., Eds. *The Hydrogen Bond*; North-Holland: Amsterdam, 1976; Vols. 1−3.

(27) (a) Speakman, J. C. *Struct. Bonding (Berlin)* **1972**, *12*, 141. (b) Novak, A. *Struct. Bonding (Berlin)* **1974**, *18*, 177. (c) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91. (d) Hadži, D. *J. Mol. Struct.* **1983**, *100*, 393.

(28) Lehman, M. S.; Larsen, F. K. *Acta Chem. Scand.* **1971**, *25*, 3859.

(29) Larsen, F. K.; Lehman, M. S.; Sotofte, I. *Acta Chem. Scand.* **1971**, *25*, 1233.

(30) Jonsson, P. G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 893.

distance is 2.215(4) Å. The sum of the C1−Cu1−O7, C1−Cu1−O9, and O7−Cu1−O9 bond angles is 353.5° (cf. the limiting values for rigorous trigonal planar and tetrahedral conformations, 360° and 328.5°, respectively). The corresponding distances and angles for the Cu2 coordination sphere are very similar. The compound $Cu(CO)(C_2H_5SO_3)$ also has a $Cu(CO)O_3$ coordination sphere, but in this compound it is more nearly tetrahedral, with three nearly equal Cu−O distances ranging from 2.050(4) to 2.068(3) Å (the sum of the three largest bond angles about the Cu^+ ion is 340.3°; the three oxygen atoms come from three triply bridging ethylsulfonate ligands).[20a] The Cu−C distance in $Cu(CO)(CH_3SO_3)$ is 1.784(8) Å,[20a] the same to within $\pm 3\sigma$ as the Cu−C distances in $Cu(CO)(H(CF_3CO_2)_2)$. The nearly equal Cu−C bond distances in the two compounds may be an indication that the $H(CF_3CO_2)_2^-$ anion is as weakly coordinating as the $C_2H_5SO_3^-$ anion, an interesting finding because trifluoroacetate is more than two pK_b units more basic than alkylsulfonates.[31]

The hydroxyl hydrogen atoms were fixed relatively close to O4 and O6 because the C3−O4 and C5−O6 bonds, at 1.287(7) and 1.285(7) Å, are longer than the other C−O distances, which range from 1.210(7) to 1.257(6) Å. The O4···O7 and O6···O10 interatomic distances are 2.636(7) and 2.622(7) Å, respectively, similar to each other as well as to the O2···O11 and O6···O9′ distances in $\{Cu_2(H(CH_3SO_3)_2)_4\}_n$. The observation that H4 and H6 are located closer to O4 than to O7 and to O6 than to O10, respectively, is consistent with the fact that the trifluoroacetate groups containing O7 and O10 are strongly bonded to two Cu^+ ions while the trifluoroacetate groups containing O4 and O6 are weakly bonded to only one Cu^+ ion.

The O4···O7 and O6···O10 distances in $[Cu(CO)(H(CF_3CO_2)_2)]_2$, indicative of moderately strong hydrogen bonds, are ca. 0.2 Å longer than the O···O distance of the very strong hydrogen bond in $KH(CF_3CO_2)_2$, which was found to be 2.437(4) Å in a neutron diffraction study.[32] The shortest, strongest O−H···O hydrogen bonds have O···O distances in the range 2.29−2.45 Å;[26,27] in these cases, the hydrogen atom is located at, or very near, the midpoint of the O···O vector and $\nu_{asym}(OH)$ is shifted to below 1000 cm^{-1}.[27] For example, $\nu_{asym}(OH)$ is 850 cm^{-1} in $KH(CF_3CO_2)_2$.[33] The other relevant compound to consider is $[CpFe(CO)_2]_2[\mu\text{-}H(Me_2C{=}CHCO_2)_2]$, in which the O···O distance is 2.406(9) Å.[18a] Schematic drawings and structural parameters for these three compounds are compared in Figure 4. It is apparent that the $H(CF_3CO_2)_2^-$ hydrogen bond is significantly weakened on changing the counterion from K^+ to $Cu(CO)^+$, an effect that is undoubtedly due to the relatively strong Cu−O bonds in $[Cu(CO)(H(CF_3CO_2)_2)]_2$ and to the asymmetric nature of the O−H···O moiety. The structure of the iron complex demonstrates that coordination of transition-metal ions to the "external" oxygen atoms of $H(RCO_2)_2^-$ ions may not always be enough to significantly lengthen the O···O distance (note that the O···O distance in the unfluorinated analogue $KH(CH_3CO_2)_2$, 2.476(8) Å,[34] is also very short); coordination of one of the "internal" oxygen atoms to the metal ion may be necessary in some cases.

Effect of CF_3COOH on the IR Spectrum of $Cu(CO)(CF_3CO_2)$ in Benzene. A benzene solution of $Cu(CO)(CF_3CO_2)$ under 1 atm of CO exhibited a ν(CO) band at 2123 cm^{-1} (the solid-state value we determined for $Cu(CO)(CF_3CO_2)$ was 2136 cm^{-1}; note that this value is nearly 20 cm^{-1} lower than the reported[20b] value of 2155 cm^{-1}). Our solid-state and solution ν(CO) values are typical for Cu(CO)(A) compounds,[35] where A^- is the conjugate base of a protic acid HA (cf. Cu(CO)Cl,[36] 2127 cm^{-1}). The fact that ν(CO) values for Cu(CO)(A) complexes are close to the value for gaseous CO, 2143 cm^{-1}, is the result of relatively strong and polar Cu←CO σ bonding and weak Cu→CO π back-bonding.[37,38] It is likely, although by no means proven, that $Cu(CO)(CF_3CO_2)$ is dimeric in benzene solution for the following three reasons. First, $Cu(CF_3CO_2)$ is dimeric in the gas phase, with the two bridging carboxylates forming a planar eight-membered Cu−O−C−O−Cu−O−C−O ring.[39] Second, $Cu(CF_3CO_2)$ was reported to form oligomers up to tetramers in benzene solution.[40] Finally, the related copper(I) carboxylates $Cu(CH_3CO_2)$[41] and $Cu(C_6H_5CO_2)$[42] were shown to be dimeric and tetrametric in the solid state, respectively. In the case of $[Cu(CH_3CO_2)]_2$, the dimeric molecules, with two Cu−O bonds per Cu^+ ions, are linked by longer, intermolecular Cu−O bonds, so that the CuO_3 coordina-

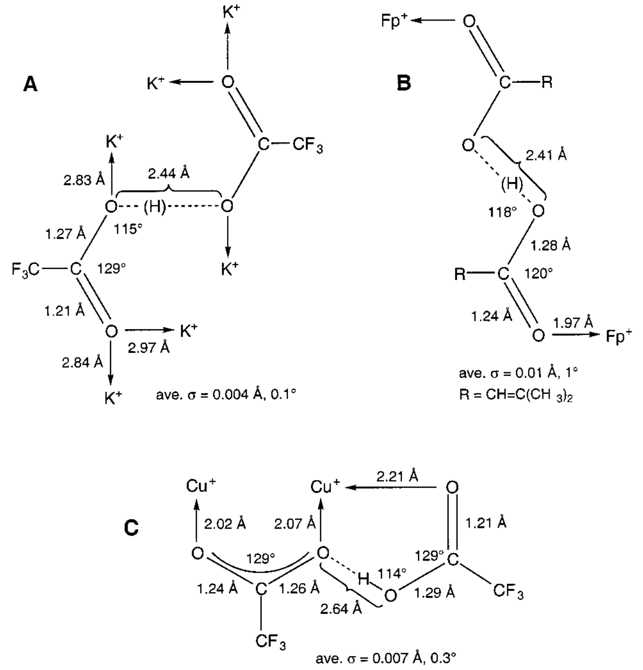


Figure 4. Drawings of the HA_2^- anions in the structures of $KH(CF_3CO_2)_2$ (**A**), $[CpFe(CO)_2]_2[\mu\text{-}H(Me_2C{=}CHCO_2)_2]$ (**B**), and $[Cu(CO)(H(CF_3CO_2)_2)]_2$ (**C**).

---

(31) (a) Guthrie, J. P. *Can. J. Chem.* **1978**, *56*, 2342. (b) Serjeant, E. P.; Dempsey, B. *Ionisation Constants of Organic Acids in Aqueous Solutions*; IUPAC Data, Series No. 23; Pergamon Press: Oxford, 1978.

(32) MacDonald, A. L.; Speakman, J. C.; Hadži, D. *J. Chem. Soc., Perkin Trans. 2* **1972**, 825.

(33) (a) Hadži, D.; Orel, B. *J. Mol. Struct.* **1973**, *18*, 227. (b) Hadži, D.; Orel, B.; Novak, A. *Spectrochim. Acta, Part A* **1973**, *29A*, 1745.

(34) Currie, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 832.

(35) (a) Bruce, M. I. *J. Organomet. Chem.* **1972**, *44*, 209. (b) Busch, M. A.; Franklin, T. C. *Inorg. Chem.* **1979**, *18*, 521. (c) Pasquali, M.; Floriani, C.; Venturi, G.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1982**, *104*, 4092.

(36) Håkansson, M.; Jagner, S. *Inorg. Chem.* **1990**, *29*, 5241.

(37) (a) Bruce, M. I. *J. Organomet. Chem.* **1972**, *44*, 209. (b) Calderazzo, F.; Dell'Amico, D. B. *Pure Appl. Chem.* **1986**, *58*, 561.

(38) (a) Strauss, S. H. *Chemtracts—Inorg. Chem.* **1997**, *10*, 77. (b) Rack, J. J.; Strauss, S. H. *Catal. Today* **1997**, *36*, 99. (c) Lupinetti, A. J.; Fau, S.; Frenking, G.; Strauss, S. H. *J. Phys. Chem.* **1997**, *101*, 9551.

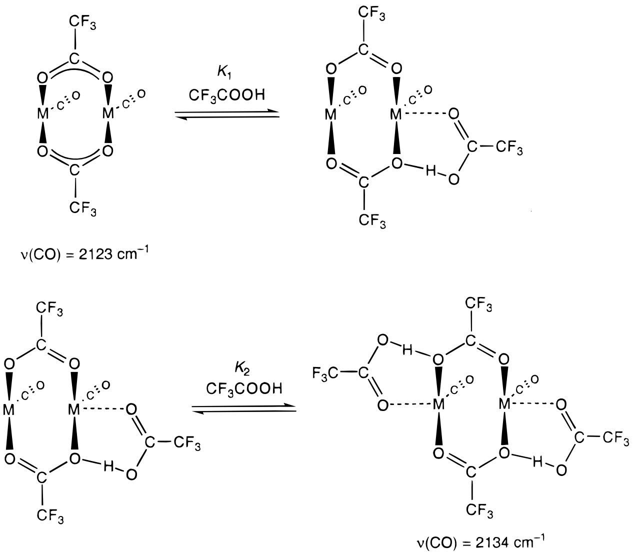
(39) Iijima, K.; Ohkawa, J.; Shibata, S. *J. Mol. Struct.* **1987**, *158*, 315.

(40) Yanagihara, N.; Sampedro, J. A.; Casillas, V. R.; Fernando, Q.; Ogura, T. *Inorg. Chem.* **1982**, *21*, 475.

(41) (a) Drew, M. G. B.; Edwards, D. A.; Richards, R. *J. Chem. Soc., Chem. Commun.* **1973**, 124. (b) Ogura, T.; Mounts, R. D.; Fernando, Q. *J. Am. Chem. Soc.* **1973**, *95*, 949. (c) Hardt, H. D.; Pierre, A. *Naturwissenschaften* **1975**, *62*, 237.

(42) Drew, M. G. B.; Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1977**, 299.

Scheme 1



tion units are planar.[41] Whether the Cu···Cu−C angles in the putative compound $[Cu(CO)(CF_3CO_2)]_2$ are closer to 90° or 180° remains to be seen.

The benzene solution of $[Cu(CO)(CF_3CO_2)]_2$ was titrated with CF_3COOH at a constant CO pressure of 1 atm. The ν(CO) band changed position, line width, and intensity during the titration, from 2123 cm^{-1} in the absence of added acid to 2134 cm^{-1} in the presence of excess CF_3COOH. Limiting spectra at 0 and 0.50 M added acid are shown in Figure S-1 (Supporting Information). The single ν(CO) band observed at all intermediate concentrations of added acid is clearly a convolution of two or more overlapping ν(CO) bands. A plot of ν(CO) vs $[CF_3COOH]$ (not shown) demonstrated that 2134 cm^{-1} is the final band position, which we assign to the structurally characterized compound $[Cu(CO)(H(CF_3CO_2)_2]_2$. A plot of the IR absorbance at 2123 cm^{-1} vs $[CF_3COOH]_{total}$ could not be fitted to a single-exponential function. Instead, the plot was fitted to a sum of two exponentials, as shown in Figure S-2 (Supporting Information). This is consistent with a model in which the acid binds to dimeric $[Cu(CO)(CF_3CO_2)]_2$ in two sequential steps, with a ratio of the two equilibrium constants equal to 8.2 (i.e., 8.2 is the ratio of the two fitted exponential multipliers). The reaction model is shown in Scheme 1. Although both dimeric compounds should in principle give rise to a symmetric and antisymmetric pair of infrared-active ν(CO) bands, the separation of the two Cu^+ ions by 3.17 Å (in $[Cu(CO)(H(CF_3CO_2)_2)]_2$) and by three-atom bridges (in both compounds) guarantees negligible kinematic or dipole coupling between the two CO oscillators. Similar dimeric structures were earlier proposed by Floriani and co-workers for compounds with the empirical formulas $Cu(CO)(CH_3CO_2)$ and $Cu(CO)(C_6H_5CO_2)$ in methanol and THF solution.[35c]

The 11 cm^{-1} increase in ν(CO) caused by the transformation of bound $CF_3CO_2^-$ to bound $H(CF_3CO_2)_2^-$ is compelling evidence that the homoconjugated hydrogen-bonded anion $H(CF_3CO_2)_2^-$ is more weakly coordinating than the parent $CF_3CO_2^-$ anion. For example, consider the ν(CO) values for the series of two-coordinate gold(I) monocarbonyls Au(CO)Cl (2162 cm^{-1}),[43] $Au(CO)OTeF_5$ (2179 cm^{-1}),[44] and $Au(CO)SO_3F$ (2195 cm^{-1}),[45] or the presumably dimeric copper(I) carbonyls $[Cu(CO)(CH_3CO_2)]_2$ (2063 cm^{-1}) and $[Cu(CO)(C_6H_5CO_2)]_2$ (2080 cm^{-1}).[35c] In general, an increase in ν(CO) results from strengthening the M−CO σ bond, increasing the partial positive charge on the metal ion, and/or weakening the M−CO π bond,[37,38] and all of these effects are caused by substituting a particular anionic donor ligand with one that is more weakly basic.

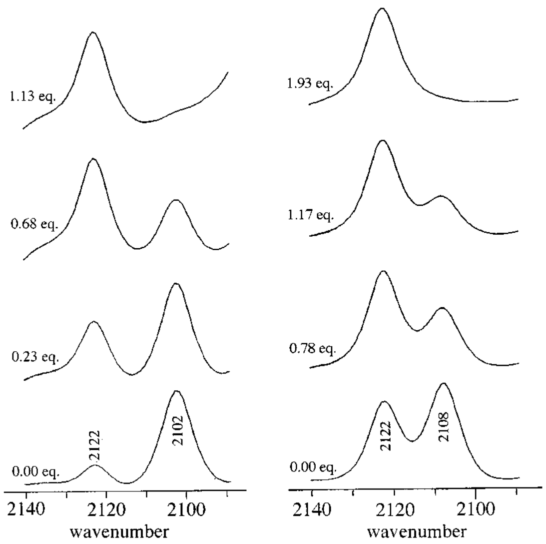


Figure 5. Infrared spectra of acetonitrile solutions of $Cu(CO)(CF_3CO_2)$ (left) and $Cu(CO)(CH_3SO_3)$ (right) with and without added equivalents of CF_3COOH and CH_3SO_3H, respectively. All solutions were under an atmosphere of CO.

Effect of HA on IR Spectra of Cu(CO)(A) Complexes in Acetonitrile. In a separate study, we have shown that simple copper(I) salts CuA dissolve in anhydrous acetonitrile under 1 atm of CO to produce solutions containing two mononuclear monocarbonyl complexes, $Cu(CO)(A)(CH_3CN)_2$ and $Cu(CO)(CH_3CN)_3^+$.[46] These two species exhibited different ν(CO) values in IR spectra, an anion-dependent ν(CO) value for $Cu(CO)(A)(CH_3CN)_2$ that ranged from 2094 cm^{-1} ($A^- = Cl^-$) to 2108 cm^{-1} ($A^- = CH_3SO_3^-$) and an anion-independent ν(CO) value of 2122 cm^{-1} for $Cu(CO)(CH_3CN)_3^+$. The higher ν(CO) value for $Cu(CO)(CH_3CN)_3^+$ is consistent with the positive charge of this species. The two species $Cu(CO)(A)(CH_3CN)_2$ and $Cu(CO)(CH_3CN)_3^+$ were found to be in mobile equilibrium for all anions A^-; dilution of the solution with additional acetonitrile while maintaining the CO pressure at 1 atm caused the intensity of the ν(CO) band due to $Cu(CO)(A)(CH_3CN)_2$ to decrease and the intensity of the ν(CO) band due to $Cu(CO)(CH_3CN)_3^+$ to increase.[46]

Figure 5 displays IR spectra of 0.05 M $Cu(CO)(CF_3CO_2)$ and $Cu(CO)(CH_3SO_3)$ in anhydrous acetonitrile under 1 atm of CO as a function of added CF_3COOH or CH_3SO_3H, respectively. In the absence of added acid, the wavenumber and the intensity of the ν(CO) band due to $Cu(CO)(CH_3SO_3)(CH_3CN)_2$ (2108 cm^{-1}) relative to the intensity of the ν(CO) band due to $Cu(CO)(CH_3CN)_3^+$ are both higher than for the ν(CO) band due to $Cu(CO)(CF_3CO_2)(CH_3CN)_2$ (2102 cm^{-1}). Both of these effects are due to the greater basicity of $CF_3CO_2^-$ relative to $CH_3SO_3^-$ (pK_a values for CF_3COOH and CH_3SO_3H are 0.5 and −1.9, respectively[31]).

In both experiments, the addition of acid HA resulted in a decrease in the intensity of the ν(CO) band due to Cu(CO)(A)-

---

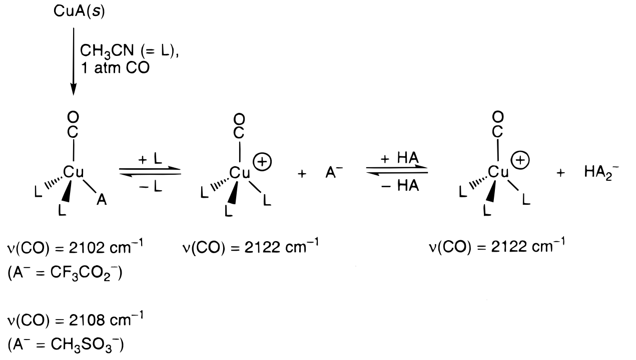
(43) Browning, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Rattray, A. J. M.; Taylor, B. F.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1977**, 2061.

(44) Rack, J. J.; Strauss, S. H. Unpublished results, 1994.

(45) Willner, H.; Aubke, F. *Inorg. Chem.* **1990**, *29*, 2195.

(46) Polyakov, O. G. Unpublished data, Colorado State University, 1998.

Scheme 2



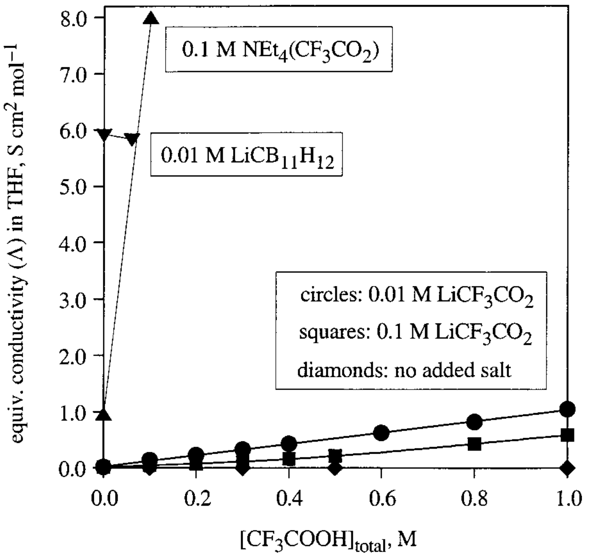


Figure 6. Equivalent conductivity vs concentration of CF_3COOH for THF solutions. The Λ value for 0.1 M $NEt_4(CF_3CO_2)$ with 1.0 M added CF_3COOH was 14.1(2) S cm^2 mol^{-1}.

$(CH_3CN)_2$ relative to the intensity of the ν(CO) band due to $Cu(CO)(CH_3CN)_3^+$. For the trifluoroacetate system, the addition of 1.1 equiv of CF_3COOH resulted in the complete disappearance of the band due to $Cu(CO)(CF_3CO_2)(CH_3CN)_2$. For the methylsulfonate system, 1.9 equiv of CH_3SO_3H was required to cause the complete disappearance of the band due to $Cu(CO)(CH_3SO_3)(CH_3CN)_2$. We propose that the addition of HA resulted in the formation of a significant amount of HA_2^- and that the decrease in the concentration of free A^- ion shifted the equilibrium between $Cu(CO)(A)(CH_3CN)_2$ and $Cu(CO)(CH_3CN)_3^+$ in the direction of $Cu(CO)(CH_3CN)_3^+$. This proposal is shown in Scheme 2. These observations are also consistent with the proposal that HA_2^- anions are significantly more weakly coordinating than their A^- precursors.

Effect of Added CF_3COOH on the Conductivity of $CF_3CO_2^-$ Salts. The results discussed above for Cu(CO)(A) vs $Cu(CO)(HA_2)$ in acetonitrile suggest that ion pairing between Li^+ and $H(CF_3CO_2)_2^-$ should also be weaker than between Li^+ and $CF_3CO_2^-$ in a given solvent. To probe this, we measured the dc conductivity of THF solutions of $LiCF_3CO_2$ as a function of added CF_3COOH. The results are listed in Table S-11 (Supporting Information) and are shown graphically in Figure 6. The equivalent conductivity (Λ value) for 0.01 M $LiCF_3CO_2$ is a linear function of the concentration of added CF_3COOH ($[CF_3COOH]_{total}$) between 0 and 1 M added acid. The Λ value at 1 M added acid, 1.05 S cm^2 mol^{-1}, is 70 times larger than the Λ value with no added acid. The Λ vs $[CF_3COOH]_{total}$ relationship is nearly linear for 0.1 M $LiCF_3CO_2$. As expected, the Λ values are higher for the 0.01 M electrolyte solution than for the 0.1 M solution.

It is well-known that the conductivity of an electrolyte solution at a finite concentration is dependent on many factors, including the relative mobilities of the ions, specific ion−solvent interactions (i.e., Lewis acid−base interactions), and a variety of solvent properties such as permittivity (dielectric constant), Lewis acidity and/or basicity, and viscosity.[47] These factors control the relative concentrations of free ions, solvent-separated ions, ion pairs, ion triplets, and higher aggregates, and these relative concentrations in turn alter the permittivity and viscosity of the solution from the permittivity and viscosity of the pure solvent. In view of these inherent complications, the goal of the present study was to demonstrate that $LiCF_3CO_2$ is more extensively ion paired in THF than $Li(H(CF_3CO_2)_2)$ and not to fully characterize and quantitate the wide variety of ionic species that are present in these solutions.

As a control experiment, we measured the conductivities of THF solutions of CF_3COOH, from 0 M added acid to 1 M added acid. For all concentrations of CF_3COOH, the observed Λ values were $\leq 5.9 \times 10^{-4}$ S cm^2 mol^{-1}, more than 10 times lower than even the lowest Λ value listed in Table 4. This demonstrates that there is no significant amount of ionization of CF_3COOH in THF at the concentrations used in this study. As another control experiment, we determined the equivalent conductivity of 0.01 M $LiCB_{11}H_{12}$ in THF and in THF containing 0.06 M CF_3COOH (the $CB_{11}H_{12}^-$ anion is an extremely weak base[1a,48]). The Λ values, 5.90 and 5.82 S cm^2 mol^{-1}, respectively, are nearly the same. The small decrease may be due to the greater viscosity of CF_3COOH ($\eta = 0.93$ cP) relative to THF ($\eta = 0.46$ cP; note that the relative permittivities of THF and CF_3COOH, 7.4 and 8.6 at 20 °C, respectively, are similar). Therefore, the addition of CF_3COOH does not, *in general*, affect the conductivity of lithium salts in THF; there must be a specific effect operating when CF_3COOH is added to THF solutions of $LiCF_3CO_2$. This effect can be understood in terms of an admittedly simple model based on the following three equilibria (all species are solvated):

$$Li^+CF_3CO_2^- \text{ (ion pair)} \overset{K_1}{\rightleftharpoons} Li^+ + CF_3CO_2^-$$

$$CF_3CO_2^- + CF_3COOH \overset{K_2}{\rightleftharpoons} H(CF_3CO_2)_2^-$$

$$Li^+H(CF_3CO_2)_2^- \text{ (ion pair)} \overset{K_3}{\rightleftharpoons} Li^+ + H(CF_3CO_2)_2^-$$

In a relatively low permittivity solvent, CF_3COOH forms a strong hydrogen bond with $CF_3CO_2^-$ (i.e., since $K_2 \gg 1$) and K_1 is relatively small. Therefore, and if $H(CF_3CO_2)_2^-$ is more weakly ion pairing than $CF_3CO_2^-$ (i.e., $K_1 < K_3$), the conductivity of a solution of $LiCF_3CO_2$ in THF should increase as the concentration of CF_3COOH increases. This is what was observed. When CF_3COOH was added to a 0.1 M solution of $NEt_4(CF_3CO_2)$, the Λ value increased much more rapidly than in the 0.1 M $LiCF_3CO_2$ experiment. However, the Λ value did not increase linearly with concentration of acid; it seemed to approach a limiting value of 14.1 S cm^2 mol^{-1} at 1 M CF_3COOH. These two observations are consistent with a much larger K_1 value for $NEt_4(CF_3CO_2)$ than for $LiCF_3CO_2$, a sensible conclusion. As further confirmation, we found that the ^1H

---

(47) (a) Barthel, J.; Gores, H. J.; Schmeer, G.; Wachter, R. *Top. Curr. Chem.* **1983**, *111*, 33. (b) Salomon, M. *J. Power Sources* **1989**, *26*, 9.

(48) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133.

chemical shift of a mixture of CF_3COOH and $NEt_4(CF_3CO_2)$ in THF-d_8 varied from the δ 13.8 for the acid to a maximum value of δ 19.0 for $H(CF_3CO_2)_2^-$ when between 1 and 2 equiv of $NEt_4(CF_3CO_2)$ was added to the solution of the acid. In acetonitrile-d_3, the limiting values were δ 11.2 and 18.7, respectively. The literature value of $\delta(^1H)$ for $[N(n\text{-}Bu)_4][H(CF_3CO_2)_2]$ at infinite dilution in chloroform-*d* is 18.2.[49]

Others have studied the effect of added protic acids on the conductivities of solutions of electrolytes. In one study, de Almeida and Inocêncio investigated the effect of added formic acid on the conductivity of $LiClO_4$ in THF.[50] They noted a linear increase in Λ with increasing mass percent of HCOOH, but they attributed this increase to an increase in dielectric constant of the medium, not to hydrogen-bond formation. In another study,[51] Kolthoff and Chantooni investigated the effect of added *p*-bromophenol (HOAr) on the conductivity of 0.002 M NEt_4Cl in acetonitrile. Interestingly, addition of the phenol decreased Λ, an effect that can be rationalized if $K_1(NEt_4Cl)$ is very large when acetonitrile ($\epsilon = 37.5$) is the solvent. In that case, addition of HOAr would not result in a larger concentration of ions but in the formation of a larger anion, $Cl\cdots HOAr^-$, with a smaller mobility. In a related study,[52] Pawlak investigated the effect of added proton donors on the conductivities of various lithium salts in sulfolane ($\epsilon = 34$). The addition of $CHCl_2COOH$ to a sulfolane solution of $KCHCl_2CO_2$ also caused a modest decrease in Λ. Apparently, the effect of added HA on the conductivity of solutions of electrolytes such as LiA and KA depends on the permittivity of the solvent used. For high-dielectric solvents such as acetonitrile and sulfolane, Λ decreases slightly because the mobility of the homoconjugated HA_2^- is less than the mobility of A^- and the electrolyte is already significantly ionized. For a low-dielectric solvent such as THF, the decreased mobility of HA_2^- is of minor importance relative to the increased concentration of "free" ions, and Λ increases as more HA is added.

Summary. We have provided clear evidence that homoconjugated HA_2^- anions are more weakly coordinating and more weakly ion pairing than their A^- counterparts. Whether HA_2^- anions are capable of serving useful roles in materials or processes that require weakly coordinating anions remains to be seen.

Acknowledgment. This research was supported by grants from the National Science Foundation (CHE-9628769 and CHE-9905482) and Air Products and Chemicals, Inc. We also thank the NIH Shared Instrumentation Grant Program for the SMART X-ray system.

Supporting Information Available: Plots of X-ray and IR data and tables listing conductivity data and detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs/acs/org.

IC991165F

---

(49) (a) Jones, R. G.; Dyer, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 2465. (b) Clark, J. H.; Emsley, J. *J. Chem. Soc., Dalton Trans.* **1974**, 1125.

(50) de Almeida, E. T.; Inocêncio, A. A. *J. Electrochem. Soc.* **1981**, *128*, 1177.

(51) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 4621.

(52) Pawlak, Z. *Electrochim. Acta* **1983**, *28*, 1659.