

# COMPLEX FORMATIONS OF SILVER(I) TRIFLUOROACETATE AND TRIFLUOROMETHANESULFONATE WITH BENZENE AND CYCLOHEXENE

NAOHISA YANAGIHARA\* and TOMIO GOTOH

Department of Materials and Science, Teikyo University, 1-1 Toyosatodai,  
Utsunomiya 320, Japan

and

TETSUYA OGURA

Department de Quimica, ICET, Universidad Autonoma de Guadalajara, A.P.1-440, Av.  
Patria #1201, Lomas del Valle, Guadalajara, Jalisco, C.P.44100, Mexico

(Received 8 January 1996; accepted 3 May 1996)

**Abstract**—An apparatus for measurements of equilibrium ligand vapor pressure has been applied in order to determine the stoichiometry of benzene and cyclohexene complexes of silver(I) trifluoroacetate ( $\text{AgCF}_3\text{CO}_2$ ) and silver(I) trifluoromethanesulfonate (silver(I) triflate,  $\text{AgCF}_3\text{SO}_3$ ) in the solid state. It has been found that the equilibrium leads the formation of such complexes as:  $(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_6)$ ,  $(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_{10})$ ,  $(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_{10})_3$ ,  $(\text{AgCF}_3\text{SO}_3)_2(\text{C}_6\text{H}_6)$ ,  $(\text{AgCF}_3\text{SO}_3)(\text{C}_6\text{H}_6)$ ,  $(\text{AgCF}_3\text{SO}_3)(\text{C}_6\text{H}_{10})$  and  $(\text{AgCF}_3\text{SO}_3)(\text{C}_6\text{H}_{10})_2$ . The temperature dependence of the gas-solid equilibrium ligand pressure has also been examined for these complexes, and the enthalpy and entropy changes according to the following complex dissociation reactions were estimated:  $(\text{AgCF}_3\text{CO}_2)_m\text{L}_m(\text{s}) \rightleftharpoons m\text{AgCF}_3\text{CO}_2(\text{s}) + m\text{L}(\text{g})$ ; and  $(\text{AgCF}_3\text{SO}_3)_n\text{L}_n(\text{s}) \rightleftharpoons n\text{AgCF}_3\text{SO}_3(\text{s}) + n\text{L}(\text{g})$ , where L's are benzene and cyclohexene. On the basis of the thermodynamic data obtained, the effects of the counter anion as well as the ligand on the complex stability are discussed. Copyright © 1996 Elsevier Science Ltd

It is well known that silver(I) as well as copper(I) complexes react with a variety of unsaturated compounds to form weakly bound  $\pi$ -complexes, and these were among the earliest  $\pi$ -complexes extensively studied.<sup>1</sup>

Although numerous olefin-silver(I) complexes have been synthesized and characterized, Ag(I) complexes are in general the least stable among transition metal  $\pi$ -complexes, as indicating the evidence of the rapid equilibrium between free and complexed olefin in solution.<sup>2</sup> The lability of silver(I) complexes are strongly dependent upon not only the counter anion involved but also upon the steric effect of substituents on the ligand and the solvation effect, and these effects have

been one of the most important strategies for the understanding of the stability of silver(I) complexes. For example, it has been revealed that the complex stability depends on the identity of the silver salt anion.<sup>3,4</sup> In hexadeuterated acetone the complex stability decreases in the anion order  $\text{SbF}_6^- > \text{BF}_4^- > \text{ClO}_4^- > \text{NO}_3^-$ . This indicates that the stronger is the acid, the more stable is the complex containing the conjugate base of the acid as anion.

Since copper(I) is isoelectronic with silver(I), we are interested in studying the coordination chemistry of both copper(I) and silver(I) salts, specially those of trifluoroacetate and trifluoromethanesulfonate. Our interest concerned the chemical species formed by those salts with simple alkenes and aromatics in the solid and liquid states. While a crystallographic study of tetrameric  $(\text{CuCF}_3\text{CO}_2)_4(\text{C}_6\text{H}_6)_2$  has been shown by Rodesiler and Amma,<sup>5</sup> we have found the monomer-

\* Author to whom correspondence should be addressed.

tetramer equilibrium of copper(I) trifluoroacetate in benzene and cyclohexene.<sup>6</sup> On the other hand, while a dimer structure of  $(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_6)$  was determined by Hunt *et al.*,<sup>7</sup> the monomeric and dimeric species of silver(I) trifluoroacetate formed in benzene and the dimeric and tetrameric species of that formed in cyclohexene were determined based on the solution equilibrium studies carried out in our laboratory.<sup>8</sup>

During the course of the studies on the related complexes, we found that both silver(I) trifluoroacetate and trifluoromethanesulfonate are capable of dissolving in poly(methylphenylsiloxane),<sup>9</sup> and these novel complexes were applied to estimate the ligand exchange equilibrium constants,<sup>10</sup> and successively employed for the separation of aliphatic, olefinic and aromatic hydrocarbons by gas chromatography.<sup>11</sup>

In continuation of our studies on silver(I) complexes, we now report the stability of the various chemical species formed by the complexation of solid silver(I) trifluoroacetate and trifluoromethanesulfonate with gaseous benzene and cyclohexene.

## EXPERIMENTAL

### General method

All chemicals used in this study were of reagent grade. Benzene and cyclohexene were distilled from calcium hydride and stored *in vacuo*. Infrared spectra were obtained as Nujol mulls with a Shimadzu FTIR-4300.

### Synthesis of silver(I) complexes

Silver(I) trifluoroacetate ( $\text{AgCF}_3\text{CO}_2$ ) and silver(I) trifluoromethanesulfonate ( $\text{AgCF}_3\text{SO}_3$ ) were prepared as follows: an excess of  $\text{Ag}_2\text{O}$  was reacted with the corresponding acid in MeOH. The mixture was filtered to remove the unreacted oxide. The solvent was then evaporated under reduced pressure. The resulting solid was recrystallized from benzene and stored *in vacuo*.

The percentage of silver in the complexes was determined by titration with a standard solution of potassium thiocyanate using potassium alum as an indicator. Found: Ag, 48.8, Calc. for  $\text{AgC}_2\text{F}_5\text{O}_3$ : Ag, 48.8, Found: Ag, 41.7, Calc. for  $\text{AgCF}_3\text{O}_3\text{S}$ : Ag, 42.0%.

### Diagram of equilibrium ligand vapor pressure and complex composition

All manipulations were carried out *in vacuo*. An apparatus similar to that previously described<sup>12</sup> was employed in these measurements. It simply consisted of a U-type mercury manometer, a capillary buret, and a reaction vessel. To the vessel containing an adequate amount of silver(I) complex aliquots of ligand ( $\text{C}_6\text{H}_6$  or  $\text{C}_6\text{H}_{10}$ ) in the capillary buret were introduced successively by a distillation. The quantity

of the ligand was calculated by the difference between the initial and the final readings of the capillary buret by a cathetometer (reading error:  $\pm 0.05$  mm). Then the whole apparatus was immersed in a water bath at a temperature controlled within  $\pm 0.02^\circ\text{C}$ . In the course of reaction, the mixture in the vessel was stirred magnetically until equilibrium was reached, and the ligand vapor pressure was monitored with the aid of the manometer and measured by the cathetometer. Thus, an equilibrium ligand vapor pressure at one fixed ligand/Ag(I) mole ratio was measured. This procedure was repeated until the necessary quantity of the ligand had been added.

## RESULTS

### Equilibrium ligand vapor pressure versus complex composition

*Benzene complexes of  $\text{AgCF}_3\text{CO}_2$  and  $\text{AgCF}_3\text{SO}_3$ .* Figure 1 shows the equilibrium pressure of benzene as a function of the mole ratio of  $\text{C}_6\text{H}_6/\text{AgCF}_3\text{CO}_2$  or  $\text{C}_6\text{H}_6/\text{AgCF}_3\text{SO}_3$  at  $30.0^\circ\text{C}$ . The presence of a single plateau at a mole ratio  $0 < \text{C}_6\text{H}_6/\text{AgCF}_3\text{CO}_2 < 1/2$  in Fig. 1(a) proves the existence of a single equilibrium in which  $(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_6)$  is formed. After it passed through this point, the equilibrium pressure increased rapidly and finally reached the pressure of free, *eg.*, non-coordinated benzene. Based on the Antoine's equation,<sup>13</sup> the vapor pressure of pure benzene at  $30.0^\circ\text{C}$  is calculated to be 119.3 mmHg, which is in good agreement with the value obtained in this measurement.

A similar pressure-composition diagram for the  $\text{C}_6\text{H}_6/\text{AgCF}_3\text{SO}_3$  system is shown in Fig. 1(b). In contrast to the evidence that the benzene complex of  $\text{AgCF}_3\text{CO}_2$  forms only one stable species, it is clearly demonstrated in Fig. 1(b) that two stable chemical species such as  $(\text{AgCF}_3\text{SO}_3)_2(\text{C}_6\text{H}_6)$  and  $(\text{AgCF}_3\text{SO}_3)(\text{C}_6\text{H}_6)$  are formed in the stepwise reaction between benzene moiety and  $\text{AgCF}_3\text{SO}_3$ . The successive addition of benzene to  $\text{AgCF}_3\text{SO}_3$  crystalline after the region where the mole ratio of  $\text{C}_6\text{H}_6/\text{Ag(I)}$  is larger than unity resulted again in a linear increase of the benzene pressure up to the vapor pressure of the pure benzene, which indicates there were no further complexations.

*Cyclohexene complexes of  $\text{AgCF}_3\text{CO}_2$  and  $\text{AgCF}_3\text{SO}_3$ .* The equilibrium pressure of  $\text{C}_6\text{H}_{10}$  at various mole ratios of  $\text{C}_6\text{H}_{10}/\text{AgCF}_3\text{CO}_2$  at  $30.0^\circ\text{C}$  is shown in Fig. 2(a). One can see clearly that there exist two plateaus at mole ratio  $0 < \text{C}_6\text{H}_{10}/\text{Ag(I)} < 1/2$  and at  $1/2 < \text{C}_6\text{H}_{10}/\text{Ag(I)} < 3/2$ . Thus, it is obvious that  $(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_{10})$  and  $(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_{10})_3$  are formed in this system, and it was found that the latter complex is gelatinous. When the mole ratio is beyond  $3/2$ , the equilibrium pressure diagram changes to be a curve instead of showing a single plateau. This behavior indicates that the solid cyclohexene complex of  $\text{AgCF}_3\text{CO}_2$  begins to dissolve gradually into

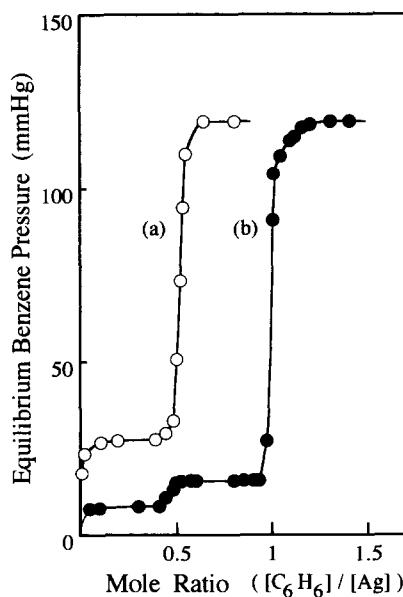


Fig. 1. Equilibrium benzene pressure at various  $[C_6H_6]/[Ag]$  mole ratios at  $30.0^\circ C$ : (a)  $AgCF_3CO_2$ ; (b)  $AgCF_3SO_3$ .

cyclohexene. Although there might exist some species in the mole ratio region over  $3/2$  up to 3, it is too ambiguous to allow unequivocal determination of the complexes present with different composition. After the mole ratio passed through 3, the pressure reached the final plateau corresponding to the pure cyclohex-

ene, and again the calculated<sup>13</sup> value of 111.1 mmHg for  $C_6H_{10}$  is consistent with that observed.

The similar diagram for the  $AgCF_3SO_3-C_6H_{10}$  system is shown in Fig. 2(b). In a similar manner as above, it is reasonably safe to say that there exist the formations of mono- and bis-cyclohexene complexes

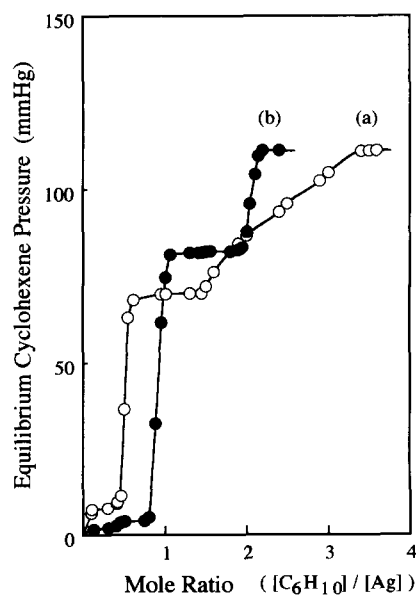


Fig. 2. Equilibrium cyclohexene pressure at various  $[C_6H_{10}]/[Ag]$  mole ratios at  $30.0^\circ C$ : (a)  $AgCF_3CO_2$ ; (b)  $AgCF_3SO_3$ .

since the diagram demonstrates clear plateau in the regions where the  $C_6H_{10}$ :Ag(I) mole ratios are 1:1 and 2:1.

#### IR spectra of the complexes

The IR spectra of the  $AgCF_3CO_2$  complexes showed characteristic absorption bands at 1680–1620, 1208–1194, 1152–1132 and 851–844  $cm^{-1}$ , which correspond to  $\nu_{as}(C=O)$ ,  $\nu_s(C-F)$ ,  $\nu_{as}(C-F)$  and  $\nu(C-C)$  of  $O_2C-CF_3$ , respectively. Since these observed values are comparable to the references earlier reported,<sup>14–16</sup> and there are virtually no changes in the frequencies of the stretching modes between the benzene and cyclohexene complexes, it is concluded that the trifluoroacetate groups act as the bridging attachment to form the polymeric structure in the all of the  $AgCF_3CO_2$  complexes studied here.

For the triflate complexes, the characteristic absorption frequencies of  $\nu_{as}(SO_3)$ ,  $\nu_s(SO_3)$ ,  $\nu_s(CF_3)$  and  $\nu_{as}(CF_3)$  were observed at 1274–1259, 1034–1031, 1256–1250 and 1178–1171  $cm^{-1}$ , respectively. Although it was too difficult to distinguish the multiplicates of the bands in particular between 1270–1250  $cm^{-1}$ , again there were no marked differences in the frequencies of the absorption bands in each triflate complex. On the basis of the studies<sup>17–20</sup> on the coordination modes of  $CF_3SO_3$ , it is reasonable to conclude that the  $CF_3SO_3$  groups in the all complexes of  $(AgCF_3SO_3)$  in this study show bridging behavior. This presumption is supported by the facts, in which the crystal structures of  $(CuCF_3SO_3)_2(C_6H_6)$ <sup>21</sup> and  $(CuCF_3SO_3)(C_6H_{10})$ <sup>22</sup> prove that both of the complexes consist of tetrameric units interconnecting by  $CF_3SO_3$  bridges to give an infinite chain.

## DISCUSSION

#### Benzene and cyclohexene complexes

The variation of the equilibrium pressure with complex composition in the system of  $AgX$  ( $X = CF_3CO_2$  and  $CF_3SO_3$ ) crystalline with gaseous ligand, L ( $L = C_6H_6$  and  $C_6H_{10}$ ), successively demonstrated the formation of the following species:  $(AgCF_3CO_2)_2(C_6H_6)$ ,  $(AgCF_3SO_3)_2(C_6H_6)$  and  $(AgCF_3SO_3)(C_6H_6)$  as the benzene complexes, and  $(AgCF_3CO_2)_2(C_6H_{10})$ ,  $(AgCF_3CO_2)_2(C_6H_{10})_3$ ,  $(AgCF_3SO_3)(C_6H_{10})$  and  $(AgCF_3SO_3)(C_6H_{10})_2$  as the cyclohexene complexes. From the point of view of their composition ratios, these complexes can be classified into 4 groups as followed: Ag(I):L ratio = 2:1, 1:1, 2:3 and 1:2. Among a great variety of Ag(I) complexes that had found in solution and in solid states, the species  $Ag_2L$ ,  $AgL$  and  $AgL_2$  are very common for olefinic ligands, but such stoichiometries are rare if the ligands are limited to benzene and cyclohexene. The crystalline complex of  $(AgCF_3CO_2)_2(C_6H_6)$  has been obtained as a dimer,<sup>7</sup> and the 2:1 complexes of  $(AgCF_3SO_3)_2(C_6H_6)$ <sup>23</sup> and

$(AgCF_3CO_2)_2(C_6H_{10})$ <sup>8</sup> have also been known to exist in the solid state. Thus, with a more careful observation of the diagram in Fig. 2(b), it is quite possible to say that a complex  $(AgCF_3SO_3)_2(C_6H_{10})$  is also formed under the experimental conditions carried out in this study, even though the change of the plateau is not so clear.

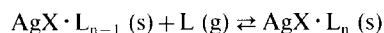
The only structures that have been known as benzene complexes of Ag(I) are the 1:1 complexes of  $(AgClO_4)(C_6H_6)$ <sup>24</sup> and  $(AgAlCl_4)(C_6H_6)$ .<sup>25</sup> With  $AgNO_3$ , cyclohexene forms 1:1 and 1:2 complexes in aqueous solution,<sup>26</sup> whereas  $(AgBF_4)(C_6H_{10})$  and  $(AgClO_4)(C_6H_{10})_2$  have been known in organic solution.<sup>27</sup> In addition, the 1:1 complex of  $AgCF_3SO_3$ : $C_6H_{10}$  in the solid state has been reported by Lewandos *et al.*<sup>28</sup> This complex shows in the IR spectrum the  $C=C$  at 1577  $cm^{-1}$ , which frequency is almost comparable with 1759  $cm^{-1}$  observed for the  $(AgCF_3SO_3)(C_6H_{10})$  obtained in this study.

The 1:2 silver(I) complexes with aromatic donors have been isolated:  $(AgClO_4)(C_6H_5C_6H_{11})$ ,<sup>29</sup>  $(AgClO_4)(C_6H_6)_2$ ,<sup>30</sup>  $(AgB_{11}CH_{12})(C_6H_6)_2$ ,<sup>31</sup> and  $(AgClO_4)(C_6H_{10})_2$ ,<sup>27</sup> in which the last one has been identified in the solution equilibrium study.

Thus, almost all chemical species found in this study are the same as or quite analogous to the similar silver(I) complexes that have been studied already both in the solid and in the solution. However, it is remarkable to note that no species such as  $(AgCF_3CO_2)_2(C_6H_{10})_3$  has been reported previously, and this unique stoichiometry might be the first example.

#### Stability of the complexes

Figures 1 and 2 show the equilibrium pressure of L as a function of the mole ratio L:AgX. In general, the stepwise formation equilibrium that is established between the solid AgX and the gaseous L can be expressed by the following reversible reaction.



Since both of those  $AgX \cdot L_n$  and  $AgX \cdot L_{n-1}$  are solids or liquids, the corresponding formation constant, K, can be defined as  $K = P_L^{-1}$ , in which  $P_L$  is the equilibrium ligand vapor pressure. Therefore, simply comparing with those  $P_L$  values, one can argue the relative stability of the complexes. Consequently, the lower the  $P_L$  value, the greater the stability.

Among the complexes formed in this study, the stability decreases in the following order:

$(AgCF_3SO_3)(C_6H_{10})$ ; 4.2 mmHg >  $(AgCF_3CO_2)_2(C_6H_{10})$ ; 7.5 mmHg >  $(AgCF_3SO_3)_2(C_6H_6)$ ; 8.2 mmHg >>  $(AgCF_3SO_3)(C_6H_6)$ ; 15.4 mmHg >  $(AgCF_3CO_2)_2(C_6H_6)$ ; 27.2 mmHg >>  $(AgCF_3CO_2)_2(C_6H_{10})_3$ ; 70.1 mmHg >  $(AgCF_3SO_3)(C_6H_{10})_2$ ; 82.1 mmHg, where the values with pressure unit are the  $P_L$  values.

Taking into account those  $P_L$  values, it is clear that

the cyclohexene complexes are in general more stable than the benzene complexes when the anion is the same, *eg.*,  $(\text{AgCF}_3\text{SO}_3)(\text{C}_6\text{H}_{10}) > (\text{AgCF}_3\text{SO}_3)(\text{C}_6\text{H}_6)$  and  $(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_{10}) > (\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_6)$ . These marked results in the complexation ability between different classes of unsaturated hydrocarbons are anticipated as a well characterized feature of them, and are roughly related to the difference in double bond characters of the unsaturated carbon-carbon bonds involved. Undoubtedly, the  $\pi$ -bond order of the isolated double bond in cyclohexene is greater than that of the double bond in benzene having the character of the delocalized  $\pi$ -electrons.

On the other hand, in the series of the above stability, it can be always expected that the Ag(I) triflate complexes are more stable than those of Ag(I) trifluoroacetate. This observation in conjunction with the early reported stability of the olefin complexes of silver(I)<sup>32</sup> establishes that the order of increasing stability parallels that of the strengths of the corresponding acids. Moreover, the  $74\text{ cm}^{-1}$  reduction in C=C stretching frequency of our  $(\text{AgCF}_3\text{SO}_3)(\text{C}_6\text{H}_{10})$  relative to free cyclohexene is larger than those for dicyclohexene- $\text{AgBF}_4$  ( $68\text{ cm}^{-1}$ )<sup>3</sup> and dicyclohexene- $\text{AgClO}_4$  ( $71\text{ cm}^{-1}$ ).<sup>33</sup> Although C=C may not be a direct measure of the strength of the coordinate bond as well as the stability, it is reasonable to assume that the differences reflect the nature of the counter anion involved.

In addition, it should be emphasized that the  $P_1$  value of  $(\text{CuCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_6)$ ,  $4.5\text{ mmHg}$ ,<sup>6</sup> is just between that of  $(\text{AgCF}_3\text{SO}_3)(\text{C}_6\text{H}_{10})$  and  $(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_{10})$ . In this case the difference of the

center metal cation rather than the anion and the ligand may play an important role in predominating the stability.

#### Temperature dependence of the equilibrium ligand pressure

The temperature dependence of the ligand in the silver(I) complexes prepared was approximated by the linear relationship:  $\ln P(\text{atm}) = -10^{-3}A/T + B$ , in the temperature range  $20.0\text{--}60.0^\circ\text{C}$ . The resultant equilibrium ligand vapor pressures at various temperatures are listed in Table 1, and  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  values for the decomposition of the complexes are summarized in Table 2. Considering that the thermodynamic data can reflect the global effect of the anion as well as the ligand on the decomposition reaction, it is quite reasonable that the  $\Delta G$  values for the complexes decrease in the aforementioned order of the stability.

It is noteworthy that the enthalpy and entropy changes accompanied in the decomposition of  $(\text{AgCF}_3\text{SO}_3)_2(\text{C}_6\text{H}_6)$  are twice as large than those of  $(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_6)$ , but there are a few differences in  $\Delta G$  values between those reactions. Hence, it may be concluded that the stability in the  $\text{AgCF}_3\text{SO}_3$  is strongly entropy controlled, and this is not the case for the complex of  $\text{AgCF}_3\text{CO}_2$ . One reason to explain the difference in this thermodynamic feature might be attributed to the difference in the crystalline packing system between them:  $(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_6)$  is known as a dimer in the crystal structure,<sup>7</sup> whereas the structure of  $(\text{AgCF}_3\text{SO}_3)_2(\text{C}_6\text{H}_6)$  is not resolved yet.

Table 1. Equilibrium ligand vapor pressure of silver(I) complexes at various temperatures

Complex	Temperature (°C)	Pressure (mmHg)	Complex	Temperature (°C)	Pressure (mmHg)
$(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_6)$	18.7	20.1	$(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_{10})$	30.0	7.5
	30.0	27.2		40.0	14.9
	40.0	38.5		50.0	24.9
	50.0	54.2		60.0	39.3
	60.0	88.8			
$(\text{AgCF}_3\text{SO}_3)_2(\text{C}_6\text{H}_6)$	17.8	4.7	$(\text{AgCF}_3\text{CO}_2)_2(\text{C}_6\text{H}_{10})_3$	30.0	70.1
	20.0	5.5		35.0	96.1
	30.0	8.2		40.0	118.3
	40.0	18.5		45.0	141.8
	50.0	37.1		50.0	170.3
	60.0	67.8			
$(\text{AgCF}_3\text{SO}_3)(\text{C}_6\text{H}_6)$	25.6	11.3	$(\text{AgCF}_3\text{SO}_3)(\text{C}_6\text{H}_{10})$	25.8	2.8
	30.0	15.4		30.0	4.2
	40.0	25.7		40.0	6.9
	50.0	44.5		50.0	11.9
	60.0	74.7		60.0	20.1
			$(\text{AgCF}_3\text{SO}_3)(\text{C}_6\text{H}_{10})_2$	20.0	56.7
				25.0	72.8
				30.0	82.1
				35.0	130.1
				40.0	144.4

Table 2. Temperature dependence of the equilibrium ligand vapor pressure in dissociation reaction of the silver(I) complexes and some thermodynamic constants at 30.0°C

Reaction	A <sup>a</sup>	B <sup>a</sup>	$\sigma^b$	$\ln P^a$ at 30°C (atm)	$\Delta H^c$ (kJ mol <sup>-1</sup> )	$\Delta S^d$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G^e$ (kJ mol <sup>-1</sup> )
(AgCF <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>6</sub> ) → 2AgCF <sub>3</sub> CO <sub>2</sub> + C <sub>6</sub> H <sub>6</sub>	3.367	7.858	8.2 × 10 <sup>-2</sup>	-3.251	28	65	8
2(AgCF <sub>3</sub> SO <sub>3</sub> )(C <sub>6</sub> H <sub>6</sub> ) → (AgCF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>6</sub> ) + C <sub>6</sub> H <sub>6</sub>	5.448	14.03	9.2 × 10 <sup>-2</sup>	-3.946	45	117	10
(AgCF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>6</sub> ) → 2AgCF <sub>3</sub> SO <sub>3</sub> + C <sub>6</sub> H <sub>6</sub>	6.158	16.01	9.9 × 10 <sup>-2</sup>	-4.306	51	133	11
(AgCF <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>10</sub> ) → (AgCF <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>10</sub> ) + 2C <sub>6</sub> H <sub>10</sub>	4.164	11.41	2.9 × 10 <sup>-2</sup>	-2.327	35	95	6
(AgCF <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>10</sub> ) → 2AgCF <sub>3</sub> CO <sub>2</sub> + C <sub>6</sub> H <sub>10</sub>	4.785	11.39	2.8 × 10 <sup>-2</sup>	-4.397	40	95	11
(AgCF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>10</sub> ) → (AgCF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>10</sub> ) + C <sub>6</sub> H <sub>10</sub>	4.496	12.72	3.4 × 10 <sup>-2</sup>	-2.113	37	106	5
(AgCF <sub>3</sub> SO <sub>3</sub> )(C <sub>6</sub> H <sub>10</sub> ) → AgCF <sub>3</sub> SO <sub>3</sub> + C <sub>6</sub> H <sub>10</sub>	5.622	13.25	8.5 × 10 <sup>-2</sup>	-5.298	47	110	13

<sup>a</sup>  $\ln P$  (atm) = -10<sup>3</sup> A/T + B ±  $\sigma$ .

<sup>b</sup> standard deviation.

<sup>c</sup>  $\Delta H$  = RA.

<sup>d</sup>  $\Delta S$  = RB.

<sup>e</sup>  $\Delta G$  = -RT ln P at 30.0°C.

However, taking into account that the structure of (CuCF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>) consists of infinite folded ladder-like polymeric chains, one may expect the similar packing role for (AgCF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>).

*Acknowledgements*—One of the authors (N.Y.) wishes to acknowledge partial support of this work by Japan Society for the Promotion of Science (JSPS) in Japan and El Consejo Nacional de Ciencia y Tecnologia (CONACYT, A9108-0512) in Mexico.

## REFERENCES

- H. W. Quinn and J. H. Tsai, *Advan. Inorg. Radiochem.* 1969, **12**, 217.
- L. J. Andrews and R. W. Keefer, *J. Am. Chem. Soc.* 1950, **72**, 3113; T. Fueno, T. Okayama, T. Deguchi and J. Fulukawa, *J. Am. Chem. Soc.* 1965, **87**, 170.
- H. W. Quinn and D. N. Glew, *Can. J. Chem.* 1962, **40**, 1103.
- W. Featherstone and A. J. S. Sorrie, *J. Chem. Soc.* 1964, 5253.
- P. F. Rodesiler and E. L. Amma, *J. Inorg. Nucl. Chem.* 1977, **39**, 1227.
- N. Yanagihara, J. A. Sampedro, R. Casillas, V. Q. Fernando and T. Ogura, *Inorg. Chem.* 1981, **21**, 475.
- G. W. Hunt, T. C. Lee and E. L. Amma, *Inorg. Nucl. Chem. Lett.* 1974, **10**, 909.
- N. Yanagihara, R. Casillas, V. F. Rodriguez, L. R. Hurtado J and T. Ogura, *Rev. Soc. Quim. Mex.* 1985, **29**, 329.
- A. M. Soto, N. Yanagihara and T. Ogura, *Anal. Chem.* 1991, **63**, 1178.
- A. M. Soto, N. Yanagihara and T. Ogura, *J. Coord. Chem.* in press.
- A. M. Soto, N. Yanagihara and T. Ogura, *J. Coord. Chem.* in press.
- J. A. Sampedro and T. Ogura, *Trans. Met. Chem.* 1976, **1**, 127.
- R. C. Reid, J. M. Prausnitz and B. E. Poling, *The Properties of Gases and Liquids*, 4th Ed. McGraw-Hill, (1987).
- C. A. Agambar and K. G. Orrell, *J. Chem. Soc. A* 1969, 897.
- M. B. Dines, *Inorg. Chem.* 1972, **11**, 2949.
- C. J. Pouchert, *The Aldrich Library of FT-IR Spectra*, 1st Ed., vol. 2, p. 1242A. Aldrich Chemical Company Inc. (1985).
- H. Bürger, K. Burczyk and A. Blaschette, *Monatsh. Chem.* 1970, **101**, 102.
- S. D. Brown and G. L. Gard, *Inorg. Chem.* 1975, **14**, 2273.
- G. A. Lawrence, *Chem. Rev.* 1986, **86**, 17 and references therein.
- J. R. Dalziel and F. Aubke, *Inorg. Chem.* 1973, **12**, 2707.
- M. B. Dines, *J. Chem. Soc. Chem. Commun.* 1973, 12.
- P. J. J. A. Timmermans and A. Mackor, *J. Organomet. Chem.* 1984, **276**, 287.
- M. B. Dines, *J. Organomet. Chem.* 1974, **67**, C55.
- H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.* 1958, **80**, 5075.
- R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.* 1966, **88**, 3243.
- J. Q. Traynham and J. R. Olechowski, *J. Am. Chem. Soc.* 1959, **81**, 571.
- J. Solodar and J. P. Petrovich, *Inorg. Chem.* 1971, **10**, 395.
- G. S. Lewandos, D. K. Gregston and F. R. Nelson, *J. Organomet. Chem.* 1976, **118**, 363.
- E. A. Hall and E. L. Amma, *Chem. Commun.* 1968, 622.
- B. G. T-Mori, D. Janjic and I. M. Vezzosi, *J. Inorg. Nucl. Chem.* 1958, **20**, 577.
- K. Shelly, D. C. Finster, Y. J. Lee, W. R. Scheidt and C. A. Reed, *J. Am. Chem. Soc.* 1985, **107**, 5955.
- H. Frye, E. Kuljian and J. Viebrock, *Inorg. Chem.* 1965, **4**, 1499.
- H. Hosoya and S. Nagakura, *Bull. Chem. Jpn.* 1964, **37**, 249.