Aromatic Complexes of Copper(I) Trifluoromethanesulphonate

By Martin B. Dines*
(*Esso Research and Engineering Company, Linden, New Jersey* 07036)
and Peter H. Bird
(*Sir George Williams University, Montreal, Quebec, Canada*)

Summary The benzene complex of copper(I) trifluoromethanesulphonate undergoes ready ligand exchange in paraffinic slurries with alkyl benzenes, whereby a unique ordering of stabilities of the complexes is manifested; a preliminary X-ray structural determination of the benzene complex is presented.

In the course of a study of the complexing properties of the benzene–copper(I) trifluoromethanesulphonate adduct,[1] rapid and dynamic equilibria were observed when the solid was mixed with alkyl benzenes [equation (1)]. The relative stabilities thus obtained were intriguing and prompted a structural determination.

$$(\mathrm{CuOSO_2CF_3})_2\mathrm{C_6H_6} + \mathrm{ArH} \underset{K_{\mathrm{eq}}}{\overset{\text{alkane}}{\rightleftharpoons}} (\mathrm{CuOSO_2CF_3})_2\mathrm{ArH} + \mathrm{C_6H_6} \qquad (1)$$

A sample of $(\mathrm{CuSO_3CF_3})_2,\mathrm{C_6H_6}$ was obtained by a slow recrystallization from benzene solution at about 70° in a sealed tube. The unit cell data are: space group $F\bar{1}$ (No. 2, non-standard setting) $a = 17{\cdot}97(1)$, $b = 19{\cdot}78(1)$, $c = 8{\cdot}828(5)$ Å, $\alpha = 94{\cdot}17(4)$, $\beta = 77{\cdot}31(4)$, $\gamma = 106{\cdot}62(4)°$, $Z = 4$. Intensity data for 1300 reflections were collected on a Picker automatic X-ray diffractometer. Structure solution by normal Patterson and Fourier synthesis methods, followed by least-squares refinement of all atomic parameters (anisotropic) other than those for hydrogen atoms led to a final discrepancy index of 8·0%. The structure, part of which is shown in Figure 1, consists of infinite chains of $\mathrm{CuSO_3CF_3}$ units (Figure 2). These chains are cross-linked in sheets by the benzene molecules. Two copper atoms are π-bonded to each ring, Cu(1) being 2·30(2) and 2·12(2) Å from C(1) and C(2), and Cu(2) being 2·09(2) and 2·12(2) Å from C(3) and C(4). Copper–oxygen distances vary from 2·00 to 2·22 Å and oxygen–sulphur distances from 1·42 to 1·47 Å. Angles between oxygen atoms subtended at the copper atoms are in the range 90·3 to 106·2°, while at the sulphur atoms, angles between atoms vary from 125·3 to 150·3°. The structure is not sufficiently well determined to observe any significant deviations of carbon–carbon distances from their values in benzene.

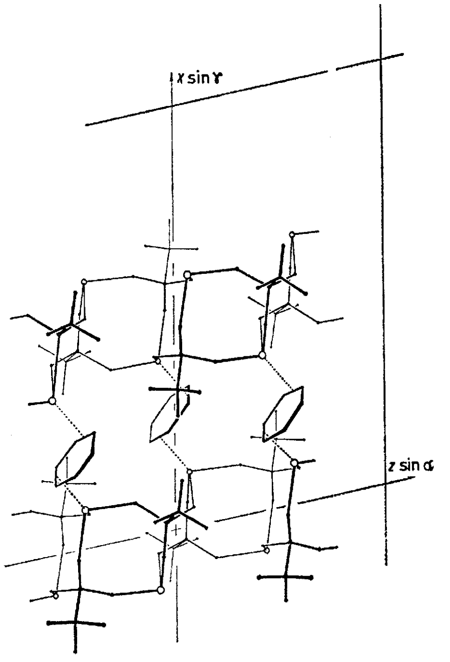

Figure 1. *Copper atoms are shown as open circles*

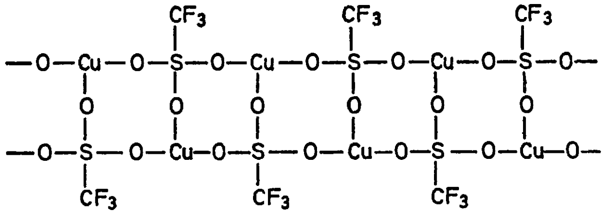

Figure 2

Representative values of K_{eq} (benzene = 1) are listed in the Table. Apparently, geometry and the size of the ring substituents predominantly dictate the stability ordering, since it does not follow established patterns of π-basicity.[2]

Table. *Relative stabilities of the aromatic complexes* $(\mathrm{CuOSO_2CF_3})_2\mathrm{ArH}$.

ArH	K_{eq}
(Benzene)	(1)
Toluene	0·7
Ethylbenzene	0·08
Cumene	0·04
n-Butylbenzene	0·05
o-Xylene	1·2
m-Xylene	0·4
p-Xylene	16·0
Mesitylene	0·03

It follows from the structure of the benzene complex that the specific situation of the aromatic rings between the inorganic chains allows for possible shape selectivity arising from the spacial restrictions therein; however at this time we cannot venture the details of such interactions with confidence. Although an analogy may be seen with the Werner type of clathration compounds,[3] the present situation is clearly not clathration, which implies the absence of strong bonding with the host material.

(*Received*, 16*th October* 1972; *Com.* 1753.)

---

[1] R. G. Solomon and J. K. Kochi, *J.C.S. Chem. Comm.*, 1972, 559.

[2] See L. J. Andrews, *Chem. Rev.*, 1954, **54**, 713; also, D. A. McCaulay, in 'Friedel–Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1964, ch. 24.

[3] For a concise review, see the Stanford Research Institute Process Economics Program Report no. 25, 'Xylenes Separation,' 1967.