# Preparation and *X*-Ray Molecular Structure of an Unusal Copper(I) Polynuclear Species: Tetrakis(copper trifluoroacetate)dibenzene

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*Summary* The preparation, some of the reactions with olefins, and the crystal and molecular structure of a unique polynuclear $Cu^{I}$–benzene complex are reported: $Cu_4(F_3CCO_2)_4 \cdot 2C_6H_6$.

COMPLEXES between copper(I) and aromatic molecules have been known for some time.[1,2] They are of interest not only from the point of view of molecular geometry and chemical bonding, but also as intermediates in the preparation and reactions of olefin complexes.[3] Copper(I)–aromatic complexes may also be used as agents for the selective separation of certain aromatic hydrocarbons.[4] We report an unusual polynuclear $Cu^{I}$–aromatic complex and some of its properties and reactions.

Reaction of trifluoroacetic anhydride with $Cu_2O$ in dry benzene at 60 °C for 1 h under nitrogen in an H-tube[2] gave crystals from the warm solution. *Crystal data*: monoclinic; $P2_1/n$; $a = 24{\cdot}581(6)$, $b = 10{\cdot}586(1)$, $c = 11{\cdot}603(2)$ Å; $\beta = 113{\cdot}13(1)°$, $\lambda = 0{\cdot}710683$ Å, $D_m = D_c = 2{\cdot}07$ g cm$^{-3}$; for $Z = 4$ ($[CuF_3C_2O_2]_4 \cdot 2C_6H_6$ units). Measurements were made on a crystal sealed in a thin-walled capillary and mounted on a Picker automated diffractometer.[5] 6972 independent *hkl* reflections were measured to $2\theta = 60°$ with Mo-$K_\alpha$ radiation, of which 2342 were statistically above background. The structure was solved by a combination of direct and heavy atom methods and refined by full-matrix least-squares with anisotropic temperature factors and including anomalous dispersion corrections to a final *R* of 0·106. This is relatively high by modern standards but there is considerable disorder in the $CF_3$ groups for which there is no straightforward compensation. Some of the fluorines are two-fold disordered, some are three-fold disordered, and some seem to have complete rotational disorder about the C–C bond. We were initially uncertain of the stoicheiometry and later, after we recognized the disorder problem, we decided an absorption correction and re-refinement would not be profitable.

The structure may be described as a planar parallelogram of four copper atoms with sides of *ca.* 2·8 Å, interior angles of 113·1°(4) and 66·8°(3), and shortest Cu–Cu distance of 3·07(1) Å. These copper atoms are held together by bridging trifluoroacetate groups (TFA) in which the $CO_2^-$ group is approximately perpendicular to the $Cu_4$ plane but adjacent carboxy-groups are on opposite sides of the plane (Figure). The Cu–O distance varies from 1·83 to 2·2 Å with the O–Cu–O angles in the range 162—175° The TFA group is normal within experimental error. The basic framework of this structure is similar to that found for $(Me_2N_3)_4Cu_4$.[6] However, the copper atoms here have a co-ordination number of three by forming $\pi$-bonds to benzene in the *meta*-positions. Both benzene molecules are canted toward the same side of the $Cu_4$ plane. The shortest Cu–C distances are in the range 2·7—3·0 Å. These distances are much longer than those in benzene–copper trifluoromethanesulphonate [2·09(2), 2·13(2) Å][4] and $C_6H_6{\cdot}CuAlCl_4$ [2·15(3), 2·30(3) Å].[2] The benzene rings show large thermal motions which precludes any meaningful discussion of aromatic ring distances. However, the long Cu–C distances and the large thermal motions of the benzene molecules indicate only weak binding of the aromatic units. This is an ideal situation for the ready replacement of aromatic molecules by olefins and consequently $Cu_4(TFA)_4{\cdot}2C_6H_6$ might be a good olefin carrier in benzene solution.

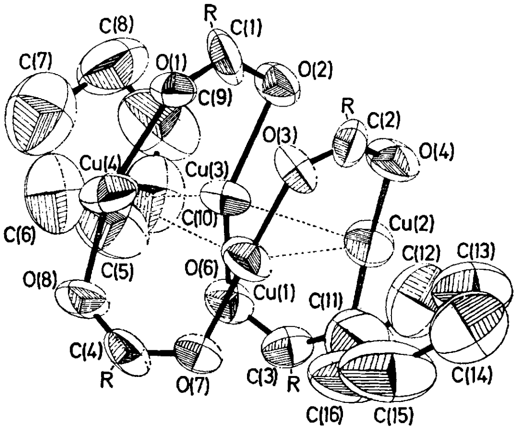

FIGURE. An ORTEP[9] drawing of the tetrakis[copper(I) trifluoroacetate]dibenzene molecule. The $CF_3$ groups are designated by R. The large thermal motions of the benzene rings are readily apparent.

At room temperature indene ($C_9H_8$) smoothly replaces benzene from $Cu_4(TFA)_4{\cdot}2C_6H_6$ in benzene solution to form a compound of stoicheiometry $Cu(TFA){\cdot}C_9H_8$. The identical compound can be prepared from the anhydride, $Cu_2O$, and indene.

Single crystals of this indene adduct were isolated: monoclinic; $P2_1$, $P2_1/m$; $a = 13{\cdot}6(3)$, $b = 20{\cdot}30(5)$, $c = 9{\cdot}28(2)$ Å, $\beta = 100(1)°$, $\lambda = 0{\cdot}71683$ Å, $D_m = 1{\cdot}60$ g cm$^{-3}$; $D_c = 1{\cdot}54$ g cm$^{-3}$; $Z = 2$ [$Cu_4(TFA)_4{\cdot}4C_9H_8$ units]. The mild reaction conditions and the unit cell size make us believe that the tetramer remains intact for the indene adduct. However, it is noteworthy that the stoicheiometry here is 1 Cu : 1 $C_9H_8$ compared to 1 Cu : $\frac{1}{2}$ $C_6H_6$. That is, it requires two olefins to replace one benzene molecule. Similar reactions occur with cyclohexa-1,4-diene and cyclohexa-1,3-diene yielding a stoicheiometry of 1 olefin : 2 Cu.

The preparation of a copper(I) trifluoroacetate carbonyl complex, Cu(TFA)CO, has been reported[7] under conditions similar to that of the benzene, indene, and diolefin compounds above. We believe that the $Cu_4(TFA)_4$ polynuclear species is the fundamental building block for all these compounds including the carbonyl adduct. The carbonyl functions as a donor in the same manner as a monolefin.

To establish more clearly the structure of the above benzene compound, we have prepared the analogous benzene compound with the monochlorodifluoroacetate anion. The structure analysis of $Cu_4[F_2ClCCO_2^-]_4{\cdot}2C_6H_6$ is underway.

It is interesting that the corresponding silver compound, $Ag(TFA){\cdot}\frac{1}{2}C_6H_6$ is structurally unrelated.[8]

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