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Preliminary communication

AROMATIC COMPLEXES OF SILVER(I) TRIFLATE

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Summary

The silver salt of trifluoromethanesulfonic acid (silver(I) triflate) forms complexes with aromatics whose solid state stoichiometries involve two salt units per organic, as does the copper analog. Both show a similar preference for *p*-xylene among the eight carbon aromatic isomers, indicative of isomorphic structures. The two Ib systems are contrasted in their behavior as slurries with aromatics.

The preparation of silver(I) triflate has been known for some time [1, 2] and its moderate solubility in benzene remarked upon in passing with no great surprise, this property being attributable to the observed ability of other silver salts of strong acids (such as the perchlorate) to be effectively solvated via electron donation from aromatic to metal ion. However, the only role of the aromatics in these previous studies of silver(I) triflate has been as a recrystallization medium, the product of which was routinely pumped free of complexed benzene. Nice white needles were thus afforded which melt at about 350°C. No one examined the benzene complex.

Our interest in this material was prompted by an investigation of the analogous copper(I) system, in particular its aromatic complexes. We found [3, 4] that copper(I) triflate undergoes complexation with aromatics having the unusual ratio of metal to organic of two. Moreover, the products were found to be relatively insoluble in aromatics; and a unique ordering of the stabilities of a series of alkyl aromatics (based apparently on shape) was ascertained from liquid—solid or vapor—solid competition experiments. An X-ray crystallographic determination of the structure of the copper—benzene complex suggested the reason for the insolubility in aromatics and the source of the strong shape selectivity. The salt portion of the complex consists of infinite folded ladder-like polymeric chains (see Fig. 1). Binding the chains together in two-dimensional sheets, and experiencing the spacially inhibiting demands of the edges of the chains (imposed chiefly by the trifluoromethyl groups on sulfur) are the

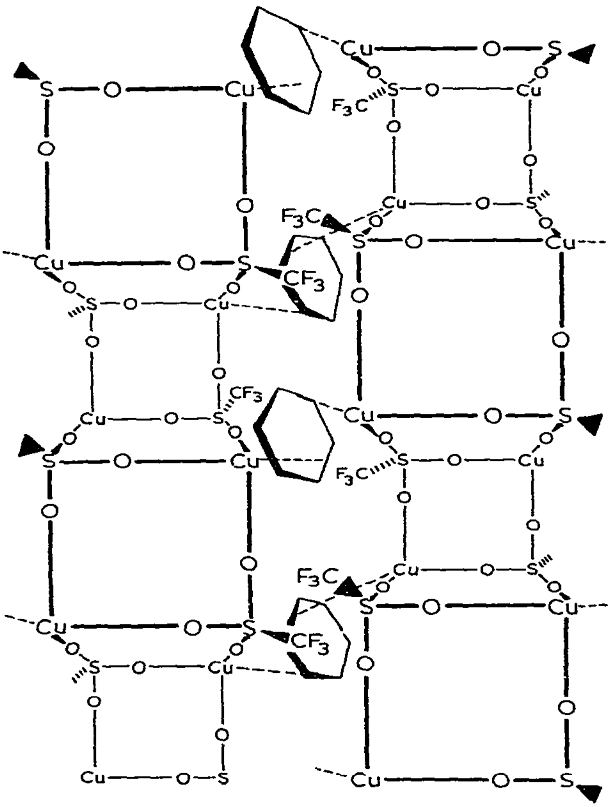

Fig. 1. Simplified depiction of the structure of the benzene complex of copper(I) triflate. For details see ref. 3.

aromatic rings. If it were found that the silver complex crystallizes in a similar structure, it would be most intriguing to gauge the effect of the 30% increase in the crystal radius on the selective behavior, keeping in mind, of course, differences in the chemistry of the two metals.

There was no a priori reason to assume isomorphic structures, as Amma's reports on the $CuAlCl_4$ [5] and $AgAlCl_4$ [6] complexes of benzene aptly demonstrate. In this case, although the configuration of the bonding between aromatic and metal ion was similar, there were gross differences in the overall crystal packing, with different coordination numbers for the two.

Preparation of the benzene complex via the reaction of silver(I) oxide and the anhydride of the parent acid in benzene was straightforward, with the addition of some pentane to assure crystallization of most of the product, which was isolated as a mat of fine white needles in high yield*. A silver analysis immediately fixed the stoichiometry of the adduct at two salt units per benzene.

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*In a typical preparation, 9.8 g (0.0347 *M*) of triflic anhydride was stirred in 60 ml benzene, then 8.0 g (0.0345 *M*) of silver(I) oxide added. The temperature rose to reflux where it was maintained for 45 minutes. On cooling the solution deposited the crystals of the complex; however an equal volume of pentane was added to increase the yield, which on filtering and drying under nitrogen amounted to 20.4 g. Analysis for $(AgSO_3CF_3)_2C_6H_6$: calcd. Ag 36.6; found 36.8%.

In a sealed capillary tube the complex liberates the benzene at about 125°C, very close to the decomposition point of the copper analog, but the bare salt remaining was white and still crystalline (unlike bare copper(I) triflate which is maroon and refractory). In the decomposition of the copper complex we postulate a degradation of the organized matrix to a three dimensional (possibly amorphous) polymer which must be extensively heated with aromatic to regenerate the white complex. Slurried in an alkane, the benzene—copper(I) triflate composition loses only a small amount (ca. 10^{-2} moles per liter) of aromatic, and can in fact be washed with pentane with little loss. Contrariwise, the silver complex will lose very nearly all of its benzene when subjected to such treatment, yielding the white bare salt.

The *p*-xylene complex of silver(I) triflate is easily preparable from the benzene complex by contacting it with *p*-xylene and in fact is much more stable as shown by the observation that pentane washing will not leech out the xylene. This behavior is manifested alone by the *p*-isomer and competitive complexation of an 8 carbon aromatic isomeric blend bears this out. In a paraffinic slurry of the silver(I) triflate—benzene complex and a mixture containing 20% *p*-xylene ca. 90% of the complexed aromatic was *p*-xylene. Such selectivity is quite similar to the copper case, however unlike copper it was shown that bare silver(I) triflate absorbs *p*-xylene with facility. As mentioned before, copper(I) triflate once stripped of complexed aromatic must be exhaustively treated to regenerate the complex.

The same stoichiometry and selectivity of the silver complex leads us to conclude that it is very likely isomorphous to the copper structure. However, the lattice energy of the silver salt is probably considerably lower as the greater solubility in benzene attests, this in spite of the fact that the silver to benzene bonding is weaker. This latter conclusion is based on the behavior in paraffins and the well established trend in the bond strengths of Group Ib metals to aromatics.

The apparent nonessentiality of regeneration of the silver complex once stripped of ligand may be due to maintainance of the structure of the matrix or to enhanced solubility which may be required in the formation of new complex.

If, in contrast to the copper complex, voids are left intact upon losing benzene one might expect little change in density in going from occupied to bare salt. In the case of copper(I) triflate we found a 14% increase in density in going from complexed to bare salt. We felt this was consistent with a collapse of the structure as delineated before. For the silver system, a 12% increase in density was observed on extraction of benzene. The latter result does not seem to be consistent with an open structure, rather it suggests the same behavior as copper.

Attempts to estimate the enthalpy of the silver to aromatic bond by measuring the change in vapor pressure of the complex as a function of temperature failed for the same reason that they were in vain for the copper system, i.e. the dissociation does not seem to be reversible in the absence of excess aromatic. This may result from the kinetic (hysteresis) effect of collapse of the voids.

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