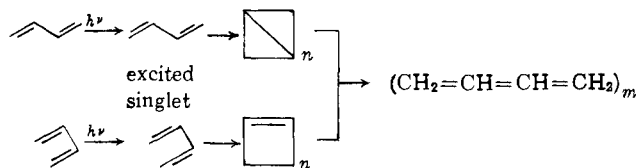


path of the internal conversion process. Since the favored conformation of 1,3-butadiene at room temperature is *trans* and since the singlet excited state is too short-lived to permit rotations, the bicyclobutane can come only from the *trans* molecules and the cyclobutene only from the *cis* molecules. Thus we can write



The predominance of cyclobutene over bicyclobutane in the products, in spite of the excess of the *trans* form of 1,3-butadiene in the reactants, may be due to the greater lability of the highly strained bicyclic compound.

The present method offers a convenient synthesis of bicyclobutane. The efficiency of the process is improved by saturating a 1% solution of 1,3-butadiene in ether with cuprous chloride before photolysis.<sup>7</sup> On irradiation with 2537-Å. light from a circular light source<sup>8</sup> for 4 days, 90% of the butadiene had disappeared. The conversion to cyclobutene was 30% while the conversion to bicyclobutane was 5 to 6%. The C<sub>4</sub> fraction was separated from the solvent by fractional distillation and each component isomer was further separated by gas chromatography. The conversion to bicyclobutane in the only step of this method is about a third of that of the final photochemical step in the earlier method.<sup>6,9</sup> The present method may also be adaptable to the synthesis of certain derivatives of bicyclobutane.

(7) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 3048 (1963).

(8) R. Srinivasan, *ibid.*, **83**, 4823 (1961). This light source is commercially available from The Southern New England Ultraviolet Co., Middletown, Conn.

(9) The conversion in ref. 6 was calculated from the statements that the decomposition of the diazo compound to yield nitrogen and C<sub>4</sub>H<sub>6</sub> was quantitative and that the ratio of 1,3-butadiene to bicyclobutane was 5:1. The over-all yield from allylacetic acid appears to be 2.6%.

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## Crystal and Molecular Structure of Metal Ion-Aromatic Complexes. I. The Cuprous Ion-Benzene Complex, C<sub>6</sub>H<sub>6</sub>·CuAlCl<sub>4</sub>

Sir:

We are carrying out a systematic investigation of chemistry, absorption spectra, and crystal structure analyses of complexes of the type C<sub>6</sub>H<sub>6</sub>·M<sup>+n</sup>(AlCl<sub>4</sub>)<sub>n</sub>, where M<sup>+n</sup> is a metal ion. We wish to report the results of a crystal structure determination of the C<sub>6</sub>H<sub>6</sub>·CuAlCl<sub>4</sub> complex.<sup>1</sup> This compound was prepared in an evacuated system from dry benzene and anhydrous, resublimed cuprous and aluminum chlorides.<sup>2</sup> Single crystals of the complex suitable for single-crystal X-ray diffraction were grown by removal of benzene and transferred into thin-walled glass capillaries which were subsequently sealed.

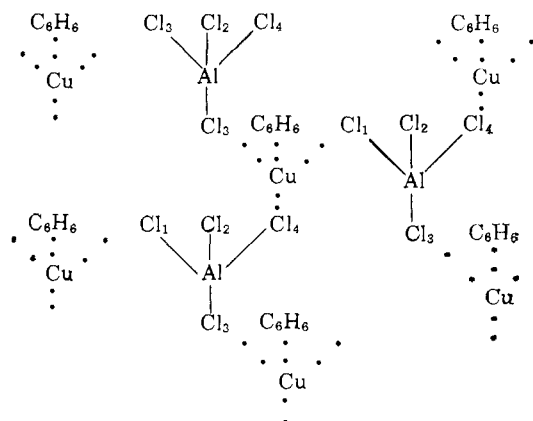
Solid C<sub>6</sub>H<sub>6</sub>·CuAlCl<sub>4</sub> was found to crystallize with 4 formula units per unit cell in the monoclinic crystal system: unit cell constants, *a* = 8.59, *b* = 21.59, *c* = 6.07 Å., β = 93°; space group P2<sub>1</sub>/n. By standard

(1) E. I. Anna and R. Turner, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, paper 30, p. 12K.

(2) Preparation, chemical, and physical properties will be reported in detail at a later date.

three-dimensional Weissenberg photographic techniques, 1200 independent *hkl* intensity measurements were made with Mo Kα radiation. The correct interpretation of the three-dimensional Patterson function gave the positions of the Cu, 4 Cl, and Al atoms. The carbon atoms were located by three-dimensional Fourier methods. Full matrix anisotropic least-squares refinement was carried out to a final reliability index,  $R_1 = \Sigma |F_o - F_c| / \Sigma |F_o|$ , of 0.139.<sup>3</sup> A final three-dimensional difference map did not indicate any unusual features.

The crystal structure is made up of infinite zig-zagging sheets composed of tetrahedral Cu(I) and AlCl<sub>4</sub><sup>-</sup>. These sheets extend indefinitely normal



to the *ab* plane and the interaction between sheets, in terms of interatomic distances, is only of van der Waals type. The Cu(I) ion is bonded to Cl atoms of three different AlCl<sub>4</sub><sup>-</sup> tetrahedra with Cu-Cl bond lengths of 2.36, 2.40, and 2.56 Å. (distance expected from sum of normal covalent radii would be 2.34 Å.). The benzene ring with Cu to center of nearest C-C bond distance of 2.13 Å. completes the coordination about the Cu(I) ion making it four coordinate. The geometry of the complex, bond lengths, bond angles, and errors can be seen in Fig. 1.

In contrast to the C<sub>6</sub>H<sub>6</sub>·AgClO<sub>4</sub> structure<sup>4</sup> where each Ag atom is bonded to two benzene rings forming an infinite chain of the type -C<sub>6</sub>H<sub>6</sub>-Ag-C<sub>6</sub>H<sub>6</sub>-Ag-C<sub>6</sub>H<sub>6</sub>-, the Cu(I) ion in C<sub>6</sub>H<sub>6</sub>·CuAlCl<sub>4</sub> is bonded uniquely to only one aromatic ring. In fact, in this case the benzene rings are back to back with normal intermolecular distances.

The charge-transfer rationale<sup>5</sup> for the nonexistence of the C<sub>6</sub> symmetry Ag<sup>+</sup>·C<sub>6</sub>H<sub>6</sub> complex (Ag<sup>+</sup> equidistant from six carbon atoms) is that the 5s acceptor orbital for Ag<sup>+</sup> is not of the correct symmetry species to interact with the benzene e<sub>1</sub> molecular orbital under C<sub>6</sub> symmetry. Further, the use of excited states of Ag<sup>+</sup> of the correct symmetry would involve 4 e.v. of excitation energy. The first of the above arguments would hold for a Cu(I)·C<sub>6</sub>H<sub>6</sub> complex as well, but Cu(0) has a relatively low lying <sup>2</sup>D state, 1.5 e.v. above the ground state, and a C<sub>6</sub> complex might be possible in this case. The results of the structure determination show that this is not the case, and further, any theory that neglects the role of the AlCl<sub>4</sub><sup>-</sup> entity is far too naïve.

The AlCl<sub>4</sub><sup>-</sup> ions presumably function as electron donors as well as the aromatic ring to the Cu(I). The Al-Cl bond lengths are 2.13, 2.14, 2.15, and 2.07

(3) Least-squares calculations were performed with the Busing and Levy ORFLS Program and errors were calculated with the Busing and Levy ORFFL Program on the IBM 7090.

(4) H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.*, **80**, 5075 (1958)

(5) R. S. Mulliken, *ibid.*, **64**, 811 (1952).

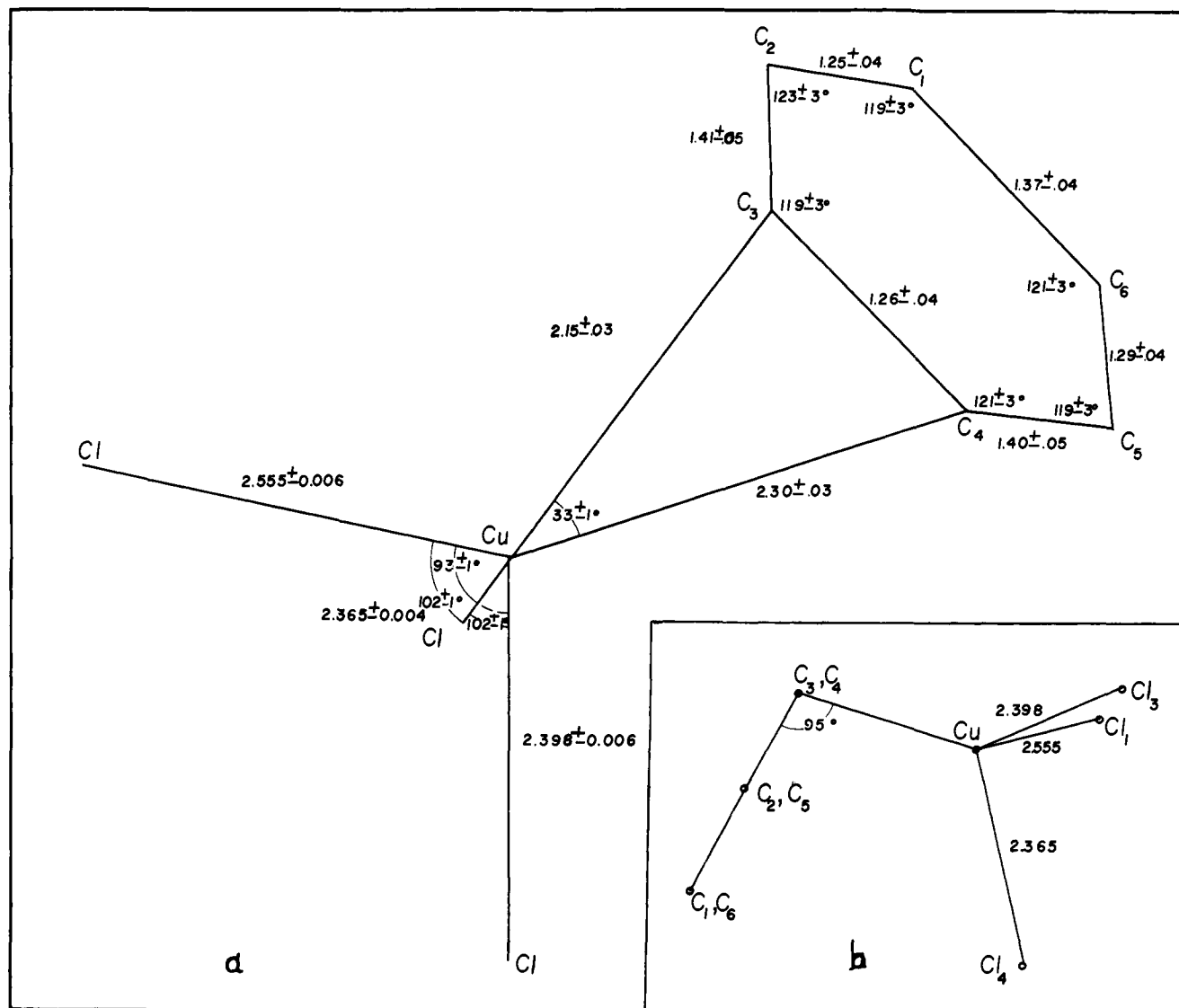


Fig. 1.—Molecular configuration of the  $C_6H_6 \cdot CuAlCl_4$  complex (all distances in Å.): a, view down the "c" axis; b, end on view of the benzene ring.

Å. with the shortest Al-Cl associated with the non-Cu coordinated Cl atom. The Al-Cl distances observed in  $Co(AlCl_4)_2^6$  varied from 2.11 to 2.19 Å., but here none of the Cl atoms could be considered as being coordinated to only an aluminum atom.

Not only is the Cu(I) ion not placed on the benzene sixfold axis, but it is also not equidistant from the two nearest adjacent carbon atoms, 2.30 and 2.15 Å. (distance expected from sum of covalent radii is 2.12 Å.). A somewhat similar situation exists in  $C_6H_6 \cdot AgClO_4$  (Ag-C, 2.49 and 2.63 Å.), but in this case the unequal metal to carbon distances manifest themselves in what appears to be a statistical disorder. The distortion of the benzene ring is toward a cyclohexatriene system with one of the short C-C bonds nearest the Cu(I). Although this ring distortion is just over the edge of statistical significance, it is worth noting that for  $C_6H_6 \cdot AgClO_4$  the C-C bonds closest to the metal ion were 1.354 Å. and the others were 1.427 Å. in length. In both these cases this bond shortening is opposite to what one might predict from simple MO or valence bond theory, and polarization forces may be the dominant factor in the bonding.

To a first approximation the Cu(I) could be considered as tetrahedral with three chlorine and one benzene acting as electron donors.

(6) J. I. Ibers, *Acta Cryst.*, **18**, 967 (1962).

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### The Polymerization of Bovine Pancreas Carboxypeptidase A<sup>1</sup>

Sir:

Only two proteolytic enzymes, chymotrypsin<sup>2</sup> and mercuripapain<sup>3</sup> are known to form a rapidly equilibrating, polymerizing system in which double boundary formation, due to the presence of polymers higher than the dimer,<sup>4,5</sup> can be observed in sedimentation experiments. This phenomenon has been observed only in *low* ionic strength buffers ( $M = 0.05$  to  $0.1$ )<sup>2,3,6</sup>

- (1) This work was carried out under NIH Grant Number HE07297.
- (2) V. Massey, W. F. Harrington, and B. S. Hartley, *Discussions Faraday Soc.*, **20**, 24 (1955).
- (3) E. L. Smith, J. R. Kimmel, and D. M. Brown, *J. Biol. Chem.*, **207**, 533 (1954).
- (4) G. A. Gilbert, *Discussions Faraday Soc.*, **20**, 68 (1955).
- (5) G. A. Gilbert, *Proc. Roy. Soc. (London)*, **A260**, 377 (1959).
- (6) L. W. Nichol and J. L. Bethune, *Nature*, **198**, 880 (1963).