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Determination by Microwave Titration of the Stoichiometry of Phosphine and Amine Complexes of Cuprous Trifluoromethanesulphonate (Copper Triflate)

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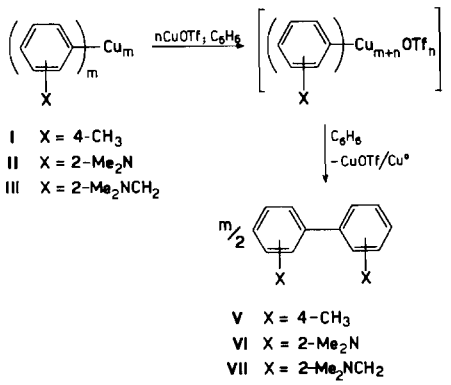
We have recently studied the interaction of arylcopper cluster compounds Ar_mCu_m (I–III) with the benzene–cuprous trifluoromethanesulphonate complex [1] $CuOTf \cdot 1/2C_6H_6$ (IV).



In some cases the formation of stable, well-defined, polynuclear complexes of the type $Ar_mCu_{m+n}OTf_n$, *e.g.* $(2\text{-}Me_2NC_6H_4)_4Cu_6OTf_2$, was observed [2]. However, more generally ArCu/CuOTf interaction led to transient formation of $Ar_mCu_{m+n}OTf_n$ species followed by intra-aggregate coupling processes which occur with high specificity [2] (quantitative formation of ArAr). The stoichiometry of the equation suggests that the reaction is catalytic in CuOTf. However, whereas *p*-tolylcopper tetramer [2] reacts quantitatively to the bitolyl V in the presence of catalytic amounts of CuOTf, total conversion of the arylcopper compounds II and III requires stoichiometric amounts of CuOTf. The fact, that contrary to V, VI and VII are potential ligands for Cu^I may account for this different behaviour. It was found that Ph_3P likewise inhibits the catalytic conversion. In order to elucidate the nature of this inhibition the complex formation of CuOTf with PPh_3, VI, VII, $2\text{-}Me_2NC_6H_5$ (VIII) and $2\text{-}Me_2NCH_2C_6H_5$ (IX) was studied.

White crystalline $(Ph_3P)_2CuOTf$ [X; m.p. 178–179 °C; found (calcd): Cu, 8.4 (8.62); F, 7.7 (7.73); C, 61.1 (60.29); H, 4.2 (4.10); P, 8.5 (8.40)%; NMR (C_6D_6, TMS, δ ppm), H_{ortho} 7.36 m(br), $H_{meta,\ para}$ 6.94 m (sharp)] was isolated in 80% yield from the 1/2 reaction of $CuOTf \cdot 1/2C_6H_6$ with Ph_3P in benzene. X exists as an undissociated monomer in benzene (mol. wt. found by cryoscopy 744: calcd. 776). IR spectroscopy of X revealed that the OTf anion has lower symmetry than C_{3v} as concluded from the splitting of the strong ν_4 (E) mode [3] (bands at 1295, 1238, and 1218 cm^{-1}) excluding an ionic structure $(Ph_3P)_2Cu^+OTf^-$. X belongs to the series of tetrahedral $CuX(PPh_3)_2$ complexes [4], in which X represents a weakly associating bidentate monoanion (ClO_4^-, NO_3^-, CF_3COO^-).

Attempts to isolate well-defined complexes of the amines VI–IX with CuOTf were complicated either by changing stoichiometries of the complexes during recrystallization or by their separation as intractable oils. However, the stoichiometry of complexes in *solution* could be detected by microwave titration [5]. The amine dissolved in benzene was added to a benzene solution of CuOTf ($1.7\text{–}4.3 \times 10^{-3}$ *M*) inside a microwave cavity [5]. The change of the transmittance curve was monitored as a function of the Cu^+/ligand ratio (see Fig. 1).

The sharp break in the $CuOTf/PPh_3$ curve *a* at 1/2 molar ratio (Cu/P) confirms the formation in solution of the 1/2 complex X. Furthermore, the formation of a weak [5] 1/3 complex $(PPh_3)_3CuOTf$ is observed in which the OTf anion most probably acts as a monodentate ligand. The 1/4 complex $(Ph_3P)_4Cu^+OTf^-$, in which the anion is forced in an outer-sphere role, is not observed. This confirms earlier conclusions [4] concerning the influence of steric requirements and donating strength of phosphine ligands on copper cationanion separation.

The titration curves *b–f* for the amines VI–IX show distinct breaks indicating that in spite of the "hard" character of the amine ligands complex formation with Cu^I does occur. This must be ascribed to the strong electron acceptor properties [1, 2] of the OTf anion which increases the electrophilicity ("hardness") of the copper cation. Indeed, complex formation does not occur with, for example, cuprous halides. The mol. ratio's at which breaks occur can be used for the deduction of the possible structures of the complexes if the number of electron-pair donating sites of the ligand and the preference of Cu^I for trigonal or tetrahedral coordination geometries is taken into account.

N,N-dimethylaniline VIII (*cf.* curve *b*) forms with CuOTf a 1/2 complex fully analogous to the phosphine complex X. Formation of this 1/2 complex is preceded by the formation of the 3/2 complex $(CuOTf)_3 \cdot (Me_2NC_6H_5)_2$. A possible structure for this complex consists of bidentate OTF anions bridging two Cu^I atoms with the anilino ligand each donating

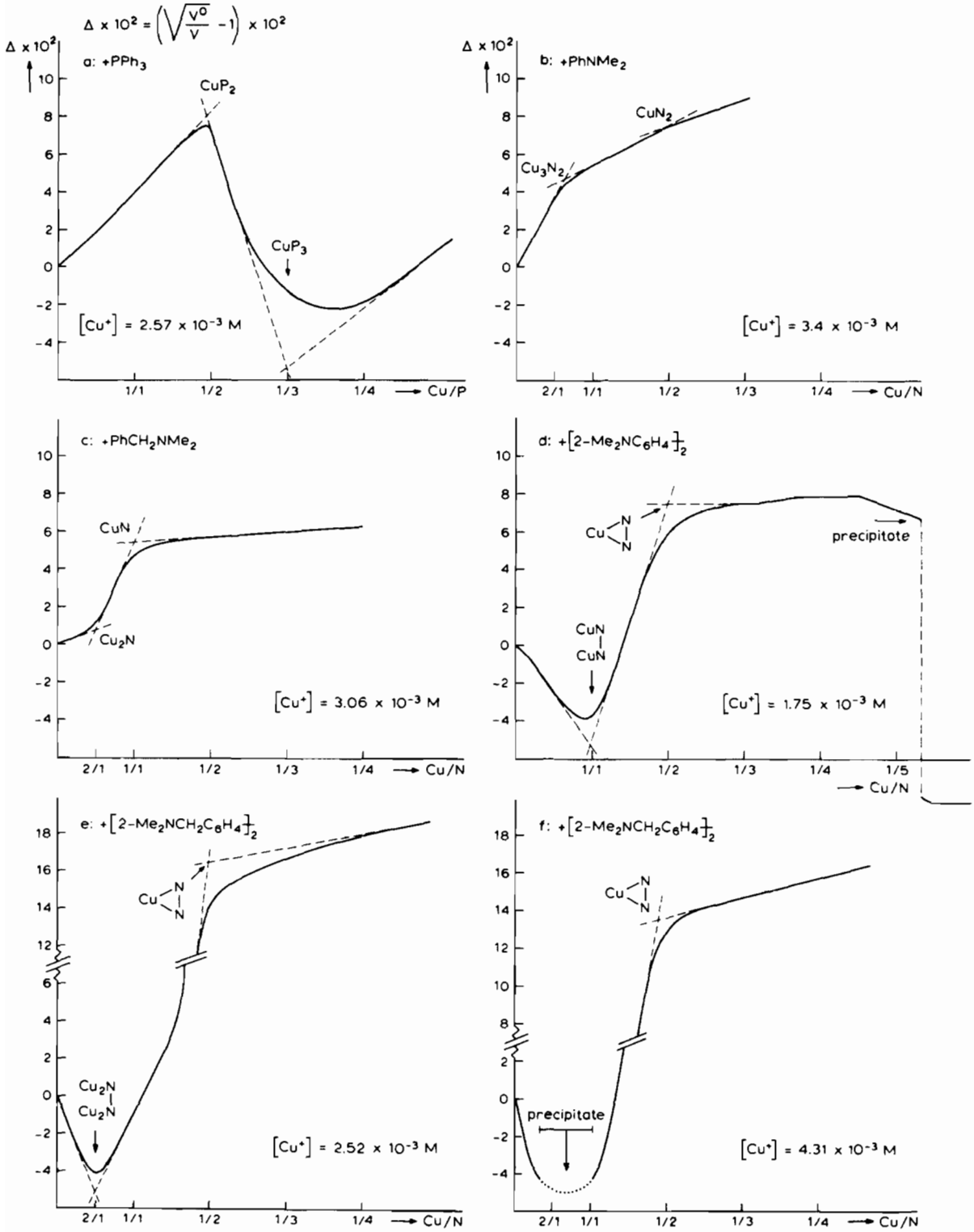


Figure 1. Microwave titration of CuOTf.

either one pair (via N) or two pairs (via N and via phenyl-π) to the polynuclear Cu^{I} unit. Such a structure has a precedent in recently published $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ which consists of bidentate O_2CCF_3 anions with each benzene molecule donating two electron pairs to te Cu_4 unit [6]. Similar

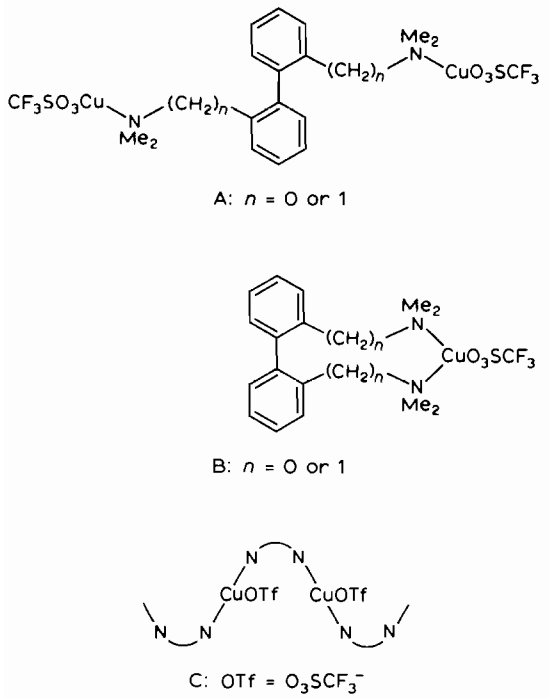


Figure 2. Structure of amine complexes of CuOTf.

polynuclear building blocks with, however, a different stoichiometry can be anticipated for the 2/1 complex $(CuOTf)_2(Me_2NCH_2C_6H_5)$ whereas for the 1/1 complex $(CuOTf)(Me_2NCH_2C_6H_5)$ intramolecular interaction of the phenyl-π system with Cu^I in addition to Cu–N coordination cannot be excluded (*cf.* curve *c*).

Curve *d* reveals the formation of the 2/1 complex $(CuOTf)_2(2\text{-}Me_2NC_6H_4\text{–}C_6H_4NMe_2\text{-}2)$ in which 2,2′-bis(dimethylamino)biphenyl, VI, coordinates with separate CuOTf units (*cf.* Fig. 2: structure A,n = 0). Upon further addition of VI the formation of a 1/1 complex is observed in which the amine most probably acts as a chelating ligand (*cf.* Fig. 2: structure B,n = 0). The nature of the white solid, which precipitates upon continued addition of VI, could not be established: either an insoluble 1/2 complex $[2\text{-}Me_2NC_6H_4)_2]_2Cu^+OTf^-$ precipitates or the soluble 1/1 complex converts into an insoluble coordination polymer in which the bidentate amine acts as a bridging ligand (*cf.* Fig. 2: C).

Two curves for the CuOTf/2,2′-bis[(dimethylamino)methyl]biphenyl(VII) interaction are shown. Curve *e* shows a break at 4/1 molar ratio pointing to the formation of a $(CuOTf)_4(2\text{-}Me_2NCH_2\text{–}C_6H_4)_2$ complex which has low solubility (*cf.* curve *f* which is recorded at higher $[Cu^+]$). Interestingly, its stoichiometry suggests that each of the $Me_2NCH_2C_6H_4$ halves acts as a bidentate ligand (via N and via phenyl-π: *cf.* the $(CuOTf)_2(Me_2NCH_2C_6H_5)$ complex in curve *c*). The second break reveals the formation of a 1/1 complex $CuOTf\cdot[Me_2NCH_2C_6H_4]_2$ in which VII acts as a chelating ligand via Cu–N coordination only (*cf.* Fig. 2: B,n = 1).

NMR spectroscopy does not provide information concerning the stoichiometry of the CuOTf complexes with amines VI, VIII and IX. Only broadened resonance patterns were observed of which the NCH_3 (and NCH_2) protons are shifted downfield by 0.1 to 0.2 ppm with respect to the free amines. However, a sharp NMR pattern was observed upon mixing CuOTf and VII in an exact 2/1 molar ratio: δ ppm in benzene-d_6 [pattern of free VII [2]]: NCH_3 2.14 and 2.32 s (coalescence at 40 °C to one s) [2.00 s]; NCH_2 2.50 and 3.86, 2 x d, J_{gem} 12Hz [3.12 and 3.20, 2 x d, J_{gem} 13Hz]; H_3 or H_6, 6.70 m [7.72 m]; other H, 6.9–7.3. In free VII the prochiral benzylic protons are anisochronous because of hindered rotation of the two phenyl rings around C_1–$C_{1'}$. Coordination of each of the NMe_2 ligands to separate CuOTf molecules (*cf.* Fig. 2: A,n = 1) enhances the activation barrier for rotation (*cf.* related processes in Sn–N coordination compounds [7]). Furthermore, Cu–N coordination renders the NMe_2 grouping a stable prochiral assembly as can be concluded from the anisochronicity of the NMe resonances. However, the NMR spectrum of the 1/1 complex in benzene-d_6 shows very broad resonances probably as a result of conformational changes of the nine-membered chelate ring (*cf.* Fig. 2: B).

The role of CuOTf–amine complexes in the inhibition of the catalytic conversion of N-substituted arylcopper cluster compounds in biaryls will be reported separately [2].

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