Inorganica Chimica Acta, 20 (1976) L42

Bis(3-Trifluoroacetylcamphorato)copper(II). Selective Formation of a Symmetrical in Preference to a Mixed Ligand Complex

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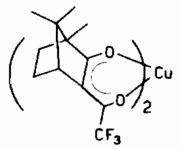
Received September 22, 1976

The importance of mixed ligand complexes in catalytic and enzymatic systems has generated considerable interest [1–3]. In general, the formation of mixed complexes has been found to be favored over corresponding symmetrical species even beyond the statistical factor [4]. This is particulary true for copper β-diketonates where the mixed complexes appear to be the major, if not exclusive, products in all cases studied to date (eq. 1) [5–7].

$$\mathrm{CuA_2 + CuB_2} \underset{\leftarrow}{\longrightarrow} \mathrm{2\,CuAB} \tag{1}$$

In sharp contrast, in an attempt to prepare Cu(hfac) (tfaCam)*, we have found the symmetrical complexes, $Cu(hfac)_2$ and $Cu(tfaCam)_2$ (*1*), to be the only detectable products.



Results and Discussion

Equimolar quantities of hexafluoroacetylacetone and 3-trifluoroacetylcamphor were stirred at 25 °C for one hour with an excess of basic copper carbonate ($CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$) suspended in chloroform. Preparative TLC (silica gel, benzene) of the chloroform-soluble material (*ca.* 85% recovery) produced two well-separated green bands. The less mobile of the two was $Cu(hfac)_2 \cdot 2H_2O$ as indicated by comparison of its mp, R_f, and visible spectrum with an authentic sample [8]. The more mobile component was identified as $Cu(tfaCam)_2$ (*1*) (possibly as a hydrate), identical in every respect to the material produced in the direct reaction of $CuCO_3$ with trifluoroacetylcamphor. After recrystallization from octane and drying at 50°/0.1 mm, *1* had the following spectral and analytical characteristics: mp 162–164°; R_f (Eastman #6060 chromatogram sheets, benzene) = 0.75; uv–vis ($CHCl_3$, nm): 260(ϵ = 1.5 × 10^4), 310(2.6 × 10^4), 330(sh), 570(43), and 665(46); *Anal.* Calcd. for $C_{24}H_{28}CuF_6O_4$: C, 51.7; H, 5.0; F, 20.4. Found: C, 51.2; H, 5.1; F, 19.7%.

That the symmetrical bis-complexes are thermodynamically favored was demonstrated by the following experiment. A $CHCl_3$ solution containing equimolar amounts of $Cu(hfac)_2$ and $Cu(tfaCam)_2$ was monitored by TLC periodically over several hours. During this time no new spots appeared – the only materials present being the starting complexes. Since Cu(II)–β-diketonate complexes have been shown to undergo rapid ligand exchange in solution to produce the more stable species [5], the mixture of bis-complexes represents the equilibrium condition.

The explanation as to why the equilibrium in eq. 1 lies to the left is not at all obvious since the comparable Cu/tfac/hfac system favors formation of the mixed complex. The present result could be due either to a particular stability associated with *1* or an instability of Cu(tfaCam) $(hfac)_2$. We cannot at this time distinguish which of these factors is dominant and firmer conclusions await continued investigation of this and related systems.

Acknowledgement

The author thanks Professors E. J. Billo, M. Clarke, and D. J. Sardella for helpful discussions, Mr. S. Souza for the preparation of trifluoroacetylcamphor, and Boston College for financial support.

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*hfac = hexafluoroacetylacetonate, tfaCam = 3-trifluoroacetylcamphorate, tfac = trifluoroacetylacetonate.