Crystal structures of difluoro[2-(4-methoxyphenyl)-3-oxo-3-phenylpropanalato]boron(III), [BF$_2$(C$_{16}$H$_{13}$O$_3$)], and bis[2-(4-methoxyphenyl)-3-oxo-3-phenylpropanalato]copper(II), [Cu(C$_{16}$H$_{13}$O$_3$)$_2$]

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The crystal structures of difluoro[2-(4-methoxyphenyl)-3-oxo-3-phenylpropanalato]boron(III), [BF$_2$(C$_{16}$H$_{13}$O$_3$)], and bis[2-(4-methoxyphenyl)-3-oxo-3-phenylpropanalato]copper(II), [Cu(C$_{16}$H$_{13}$O$_3$)$_2$], have been determined by single-crystal X-ray diffraction methods. The structures were solved by direct methods and electron density calculations and were refined by the full-matrix least-squares method. Difluoro[2-(4-methoxyphenyl)-3-oxo-3-phenylpropanalato]boron(III) crystallizes as yellow rhombs in the monoclinic space group $P2_1/c$ with $a = 11.429(3)$, $b = 11.364(4)$, $c = 11.412(4)$ Å, $\beta = 92.19(2)^\circ$, $V = 1481.0(8)$ Å$^3$ and $Z = 4$. A total of 2754 unique reflections were collected. Of these 1342 were considered observed ($I > 3\sigma(I)$) leading to a final $R$-value of 0.045. Boron is tetrahedrally coordinated to the two fluorine atoms and to two oxygen atoms of the bidentate 2-(4-methoxyphenyl)-3-oxo-3-phenylpropanalato ligand, C$_{16}$H$_{13}$O$_3$. Average bond distances: C--C (aromatic) 1.378(10) Å, B--O 1.473(7) Å, and B--F 1.343(4) Å.

Bis[2-(4-methoxyphenyl)-3-oxo-3-phenylpropanalato]copper(II) crystallizes as dark yellow-green plates in the monoclinic space group $C2/c$ with $a = 23.410(7)$, $b = 13.856(3)$, $c = 8.039(3)$ Å, $\beta = 101.79(2)^\circ$, $V = 2553(1)$ Å$^3$ and $Z = 4$. Of the unique set of 3076 scanned reflections 2401 had $I > 3\sigma(I)$ for which $R$ became 0.040. Copper is coordinated to four oxygen atoms, two from each of the two bidentate 2-(4-methoxyphenyl)-3-oxo-3-phenylpropanalato ligands, in a distorted square planar manner. The molecule has $C_2$ symmetry. Average bond distances: C--C (aromatic) 1.383(6) Å and Cu--O 1.896(8) Å. The crystals of both compounds consist of monomeric molecular complexes held together by van der Waals forces.

Introduction

Acid-catalyzed rearrangement of chalcone oxides constitutes the key step in a synthetic method for the preparation of model compounds representative of structural elements in lignins of the β-1 and β-5 types (Ahvonen et al., 1983; Brunow and Lundquist, 1984; Kristersson and Lundquist, 1980). Modifications and applications of this synthetic approach to compounds of the topical types have been published by several authors (see, e.g., Ede et al., 1987; Ralph et al., 1987; Tanaka et al., 1989; Yasuda, 1985; Yasuda et al., 1986). It is important to perform the acid treatment under suitable conditions to obtain a high yield of the desired 2,3-diaryl-3-oxopropanal intermediates. Boron trifluoride etherate has been used as catalyst for the rearrangement of the chalcone oxides. In this case the rearrangement products are obtained as complexes of type 1. Such complexes have been prepared and examined by House (1956) and House and Ryerson (1961). We have extended these studies by determining the crystal structure of such a boron complex, namely, 1. Our interest

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in this type of compounds emerges not only from the fact that they are intermediates in the aforementioned syntheses of lignin model compounds but also from the fact that they represent a comparatively rare class of compounds. In connection with the examinations of the boron complexes, House (1956) prepared the corresponding copper complexes. We have prepared a copper complex from the boron complex 1, namely, compound 2. Although copper complexes with 2,3-diaryl-3-oxo-propanalato ligands have been known since 1911 (Wislicenus and Ruthing, 1911) no crystal structures of such compounds have been reported. A determination of the crystal structure of copper complex 2 is included in this paper.

Experimental

Difluoro[2-(4-methoxyphenyl)-3-oxo-3-phenylpropanalato]boron(III) (1) was prepared according to the method described by House and Ryerson (1961). The compound melts at 149.5-151 °C (House and Ryerson, 1961).

bis[2-(4-Methoxyphenyl)-3-oxo-3-phenylpropanalato]copper(II) (2) was prepared largely according to procedures used by House (1956) for the preparation of analogous compounds. Boron complex 1 (0.2 g) was dissolved in 10 ml dichloromethane, and the resulting solution was shaken with 50 ml of a saturated solution of copper(II) acetate in water. Rhombic yellow-green plates of bis[2-(4-methoxyphenyl)-3-oxo-3-phenylpropanalato]copper(II) formed on standing, m.p. ca. 230 °C (dec.).

Crystal data and conditions for the data collection, structure determination and refinement are given in Table 1. Rotation and Weissenberg photographs (Cu Kα radiation) were taken of the X-ray diffraction patterns from 1 and 2. From these, symmetry and approximate cell dimensions were derived. Intensity data were recorded with a Syntax P21, X-ray diffractometer (graphite-monochromated Mo Kα radiation). The intensities were corrected for Lorentz and polarization effects and, for 2, absorption. The unit cell dimensions were determined from a least-squares fit of refined diffractometer setting angles for 15 reflections.

Structure determination

The structures were solved by direct methods using the program MITHRIL (Gilmore, 1984) and by electron density calculations.

Results and discussion

Atomic fractional coordinates and thermal parameters are given in Table 2 for the boron complex 1 and in Table 3 for the copper complex 2. Table 4 lists bond