The Synthesis and Characterization of Copper(II) Squarate Chloride

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(Received August 31, 1987)

Abstract

Copper(II) squarate chloride $[Cu(H_2C_4O_4)(Cl)]_2$, C_3H_7OH has been synthesized by reacting propan-2-ol solutions of $CuCl_2 \cdot 2H_2O$ and squaric acid in an inert atmosphere. The complex has been characterized by elemental analysis, spectral analysis and magnetic measurements.

Introduction

Attempts to synthesize copper(II) squarate chloride from ethanolic solutions in a manner similar to the synthesis of iron(II), nickel(II) and cobalt(II) squarate chlorides failed [1,2]. However, a brown, four-coordinate copper(II) complex was produced when propan-2-ol was used as the solvent.

Experimental

200 ml volumes of hot, degassed 1.3×10^{-2} M squaric acid (obtained from Aldrich) and 1.3×10^{-2} M $CuCl_2 \cdot 2H_2O$ solutions in propan-2-ol were mixed and allowed to stand in a nitrogen atmosphere. The method of collection and drying of the complex is similar to that described before [1]. Yield: 0.19 g (30%). *Anal.* Found: C, 26.99; H, 3.47; Cl, 14.10; Cu, 25.70. Calc. for $C_{11}H_{12}O_9Cl_2Cu_2$: C, 27.16; H, 2.47; Cl, 14.61; Cu, 26.13%.

The IR spectrum between 4000 and 600 cm^{-1} was recorded on a Perkin-Elmer 983 spectrophotometer using Nujol as the mulling agent while the spectrum between 600 and 250 cm^{-1} was recorded on a Perkin-Elmer 180 spectrophotometer using a CsBr disc. The UV–Vis reflectance spectrum was done on a Perkin-Elmer 330 spectrophotometer. The magnetic moment was done on a Newport magnetic balance using $Hg[Co(SCN)_4]$ as standard.

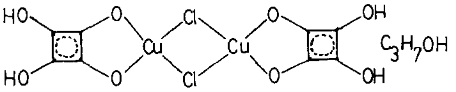
The C, H analyses were done by Huffman Laboratories, Inc., Colorado, U.S.A. and the copper determination with a Pye-Unicam SP9 atomic absorption spectrophotometer. The chloride analysis was done by Schwarzkopf Microanalytical Laboratory, New York, U.S.A.

Results and Discussion

The IR spectrum of the complex is similar to those of the squarate chlorides synthesized from ethanolic solutions [1,2]. Two major differences are the sharpness of the O–H stretch at 3470 cm^{-1} and the absence of the C=O stretch in the IR spectrum of copper(II) squarate chloride. The sharpness of the O–H stretch in the complex is assumed to be due to the absence of hydrogen bonding since the keto groups through which such bonding occurs in the squarates are apparently utilized in coordination to the copper atoms. The band due to a C=C conjugated system [3] occurs at 1580 cm^{-1} while the squarate C–C and C–O stretch vibrations occur around 1500 cm^{-1} [4,5]. The absorptions of the propan-2-ol of the crystallization occur as a multiplet around 1100 cm^{-1} [6]. Other typical squarate bands and the O–H bonded deformation occur between 600 and 940 cm^{-1} while the bridging chloride absorptions occur at 260, 274 and 286 cm^{-1}, respectively [2,7].

The UV–Vis spectrum shows a broad band between 8000 and 16 700 cm^{-1}. This band is located in the region where tetrahedral copper(II) compounds with distortion towards a square absorb [8].

The following structure is suggested:



The room temperature magnetic moment of the complex is 2.00 BM which is within the range expected for tetrahedral copper(II).

Contamination by water molecules in the lattice spaces is assumed responsible for the poor hydrogen analysis [1,2,9].

Acknowledgements

L.A.H. wishes to thank Professor Brice Bosnich and others at the University of Toronto who helped in obtaining the spectra.

0020-1693/88/$3.50

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