Synthesis and Crystal Structure of Three Mixed-Ligand Copper(II) Complexes with Nitrilotriacetic Acid

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Abstract—The synthesis and X-ray diffraction study of three Ca[CuX(Nta)]·2H₂O complexes, where X = Cl (I) or Br (II and III) are the monoclinic and orthorhombic modifications, respectively, are performed. Structures I–III are built of [CuX(Nta)]²⁻ anionic complexes and hydrated Ca²⁺ cations, which are linked by Ca–O bonds into a three-dimensional framework. In I–III, the coordination of the Cu atom includes the N atom and three O atoms of the tetradentate chelate Nta²⁻ ligand and the X⁻ anion in the trans position with respect to N. The Cu–O bond lengths vary in the ranges 1.971–2.268 Å in I, 1.958–2.289 Å in II, and 2.040–2.110 Å in III. The Cu–X bond lengths are 2.223, 2.364, and 2.354 Å in I, II, and III, respectively. In I and II, the coordination polyhedron of the Cu atom is approximated by a distorted square pyramid with an O atom at the apical vertex, whereas in III, the polyhedron is described as a distorted trigonal bipyramid with the N and Br atoms at the axial sites. The structures are additionally stabilized by O(w)–H···O and O(w)–H···X hydrogen bonds.

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INTRODUCTION

In the course of systematic structural studies of transition metal compounds with polydentate ligands, namely, monoaminopolycarboxylic acids, the synthesis and X-ray diffraction study of three mixed-ligand copper(II) complexes with nitrilotriacetic acid [H₃Nta=N(CH₂COOH)₃] were performed.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Synthesis

Calcium carbonate CaCO₃ was added in portions to a hot solution containing CuCl₂ and H₃Nta in a 1 : 1 molar ratio. The reaction mixture was filtered and evaporated at room temperature. First, a blue crystalline residue (presumably, Ca[Cu(H₂O)(Nta)]₂) appeared, and then, greenish blue prismatic crystals of Ca[CuCl(Nta)]·2H₂O (I) precipitated. Crystals I suitable for the X-ray diffraction study were obtained by recrystallization of the mixture from a hot 0.5 mol/l CaCl₂ solution.

Portions of Ca[Cu(H₂O)(Nta)]₂ with minimal impurities of the chloro complex were recrystallized from a 0.5 mol/l CaBr₂ solution. A mixture of blue and green prismatic crystals was obtained and identified in the X-ray diffraction study as the monoclinic (II) and orthorhombic (III) modifications of Ca[CuBr(Nta)]·2H₂O, respectively.

X-ray Diffraction Study

The crystal data and experimental parameters for compounds I–III are summarized in Table 1.

Experimental sets of diffraction data for crystals I–III were obtained on a CAD4 four-circle automated diffractometer at room temperature (λ=MoKα, graphite monochromator, 0 scan mode).

Structures I–III were solved by the direct method (SHELXS97) [1]. All H atoms were located from difference electron-density syntheses. The structures were refined by the full-matrix least-squares procedure on F² (SHELXL97) [1] in the anisotropic approximation for all the non-hydrogen atoms and in the isotropic approximation for the H atoms. The hydrogen atoms of the (w) water molecule in II and both water molecules in III were refined within a riding model with the isotropic thermal parameters U_H exceeding the U_eq values of the corresponding oxygen atoms by a factor of 1.2. Structure II was refined with allowance made for the secondary extinction (x = 0.062(3)). The data were corrected for absorption by crystals I–III using the ψ scan method [2].
Selected interatomic distances and bond angles in structures I–III are listed in Table 2.

The crystallographic data for compounds I–III have been deposited with the Cambridge Structural Database (CCDC nos. 268952–268954).

RESULTS AND DISCUSSION

The \([\text{CuX(Nta)}]^{2-}\) mononuclear anionic complexes and hydrated Ca\(^{2+}\) cations form the base of structures I–III (Figs. 1–3). Crystals I also contain crystallization water molecules.