

CRYSTAL STRUCTURE AND ELECTRONIC FEATURES OF A TRIS(1,10-PHENANTHROLINE)COPPER(II) NITRATE-4-NITROANILINE COMPLEX

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Abstract

A discrete copper(II) complex, tris(1,10-phenanthroline)copper(II) bis(nitrate)-4-nitroaniline, was structurally characterized to establish its coordination environment and solid-state organization. The Cu(II) centre is chelated by three 1,10-phenanthroline ligands, forming a six-coordinate, distorted octahedral CuN₆ environment. The nitrate ions and 4-nitroaniline molecule remain outside the primary coordination sphere and contribute to the crystal packing through intermolecular interactions. Electronic-structure analysis further reveals that the conjugated phenanthroline framework and heteroatom-containing groups make substantial contributions to the frontier electronic characteristics of the complex.

Introduction

1,10-Phenanthroline is a rigid N,N'-chelating ligand widely used in coordination chemistry because its aromatic framework provides strong metal binding and well-defined coordination geometries [1]. Copper complexes containing phenanthroline derivatives have attracted considerable attention owing to their structural diversity and distinctive electronic and redox properties [2]. In particular, tris(1,10-phenanthroline)copper(II) species provide useful systems for examining the relationship between metal coordination, ligand-field effects, and molecular electronic structure [3]. The solid-state organization of such complexes is also strongly influenced by counter-ions and intermolecular contacts involving aromatic and heteroatom-containing groups [4]. Nitro-substituted aniline molecules are of particular interest because their amino and nitro functionalities provide complementary hydrogen-bond donor and acceptor sites that can affect crystal packing [5]. In this work, the crystal structure and electronic features of tris(1,10-phenanthroline)copper(II) bis(nitrate)-4-nitroaniline are examined, with particular attention to the CuN₆ coordination environment, the arrangement of the outer-sphere components, and the distribution of frontier electronic density.

Keywords; *Copper(II) complex, 1,10-phenanthroline, 4-nitroaniline, crystal structure, electronic structure*

Crystal-Structural and Electronic Analysis

Single-crystal analysis shows that the compound crystallizes as a discrete tris-chelated Cu(II) species with the formulation Cu(phen)₃(NO₃)₂·4-NO₂C₆H₄NH₂. The Cu(II) centre is surrounded by three 1,10-phenanthroline ligands, each acting as a bidentate N,N' donor, resulting in a six-coordinate environment with a distorted octahedral geometry (Fig. 1). The chelating phenanthroline ligands form a rigid

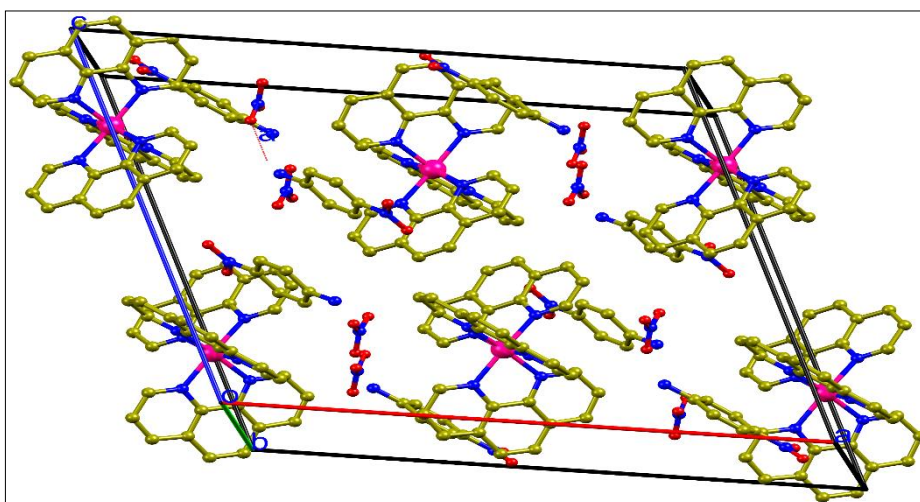
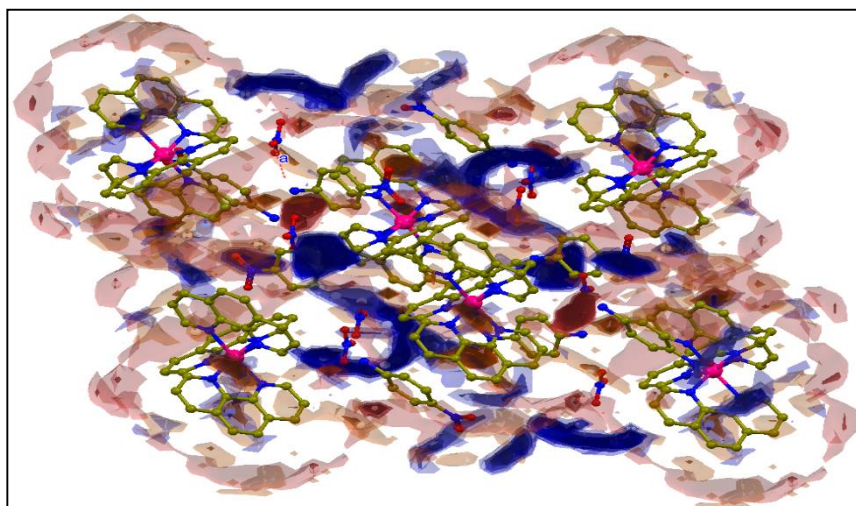


Fig. 1. Crystal packing arrangement of tris(1,10-phenanthroline)copper(II) bis(nitrate)-4-nitroaniline, showing the coordination environment of the Cu(II) centre and the spatial arrangement of nitrate and 4-nitroaniline molecules.

aromatic shell around the metal centre and restrict direct access to Cu(II), while the nitrate ions occupy the outer coordination sphere. The 4-nitroaniline molecule is also non-coordinating and is retained as a separate molecular component of the crystal. Its amino and nitro functionalities provide potential hydrogen-bond donor and acceptor sites, respectively, which may contribute to the packing arrangement together with C–H···O contacts and aromatic $\pi\cdots\pi$ interactions. The unit-cell packing shown in Fig. 1 demonstrates the separation of the cationic complexes by the nitrate and 4-nitroaniline components.

Fig. 2. Calculated molecular-orbital distribution of tris(1,10-phenanthroline)copper(II) bis(nitrate)-4-nitroaniline, illustrating the spatial distribution of electron density within the complex.

The calculated molecular-orbital distribution presented in Fig. 2 shows that the frontier electronic



density is mainly associated with the conjugated phenanthroline framework and heteroatom-containing groups. This distribution indicates that the ligand environment plays an important role in defining the electronic characteristics of the complex, while the sterically protected Cu(II) centre is embedded within the three-dimensional ligand framework.

Conclusion

The structural investigation establishes tris(1,10-phenanthroline)copper(II) bis(nitrate)-4-nitroaniline as a discrete copper(II) complex in which three bidentate 1,10-phenanthroline ligands define a distorted

octahedral CuN₆ coordination environment. The nitrate ions and 4-nitroaniline molecule are not directly coordinated to the copper centre and occupy the outer structural region of the crystal. Their presence, together with the rigid aromatic phenanthroline ligands, contributes to the overall molecular packing through non-covalent intermolecular contacts. The electronic-structure analysis indicates that the conjugated phenanthroline framework and heteroatom-rich regions are important contributors to the frontier electronic characteristics of the compound.

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