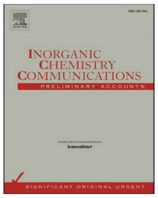
Inorganic Chemistry Communications 183 (2026) 115873

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche



Research Article

Synthesis, spectroscopic and single-crystal analysis, and DFT studies of N_2O_2 diamine coordination complexes: solvent-driven geometry switching and NLO properties

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ARTICLE INFO

Keywords:
Tetradentate N_2O_2 ligand
Diamine-based complexes
X-ray crystallography
Solvent-driven geometry transformation
DFT studies
Nonlinear optical properties

ABSTRACT

The design of coordination compounds with solvent-responsive optical properties remains a central challenge in molecular photonics. Here, we describe the synthesis and full characterisation of a symmetrical tetradentate diamine ligand, 3,3′-((1,2-phenylenebis(azanediyl))- bis(methanylylidene))bis(pentane-2,4-dione) (H_2L), and its neutral square-planar complexes [M(L)] (M(II) = Co, Ni, Cu). The Cu(II) complex crystallised as [Cu(L)]·0.5 (pyrazine), adopting a nearly square-planar geometry ($\tau_4 = 0.06$) in the solid state, as confirmed by single-crystal X-ray diffraction. In DMSO solution, UV–Vis spectra revealed reversible axial coordination of two solvent molecules, driving a transformation to a distorted octahedral geometry. Structural assignments were supported by FT-IR, UV–Vis, NMR, ESI-MS, conductivity, and magnetic susceptibility measurements. Density functional theory (DFT) calculations (B3LYP/6-311 + G(d,p) for H_2L; LANL2DZ for the complexes) reproduced the experimental geometries, mapped frontier orbital distributions, and yielded global reactivity descriptors. Among the complexes, [Cu(L)] displayed the narrowest HOMO–LUMO gap ($\Delta E = 3.911$ eV), the highest polarisability ($\alpha = 305.3$ a.u.), and an exceptionally large second-order hyperpolarisability ($\beta = 2.20 \times 10^4$ a.u.), surpassing benchmark compounds such as urea, *p*-nitroaniline (pNA), and 2-methyl-4-nitroaniline (MNA) by more than 50 %. These results highlight diamine-derived N_2O_2 frameworks as promising candidates for solvent-responsive nonlinear optical (NLO) materials, combining hydrolytic stability with geometry switching and enhanced second-order optical performance. Importantly, X-ray data reveal that coordination to Cu(II) induces electron redistribution, imparting imine-like character to the nitrogen donors despite the diamine nature of the free ligand. This interplay highlights both the novelty and the performance advantage of the present system within the second-order NLO domain of Cu(II) complexes.

1. Introduction

Coordination chemistry has grown steadily in recent decades, reflecting the sustained importance of metal-based compounds in science, technologies, and industry. This growth has closely followed progress in synthetic organic chemistry, which continues to inspire new and more efficient methods of synthesis [1–3]. Much of this work is directed toward designing and improving pathways for small organic molecules containing donor atoms that act as coordination centres [4–7]. The synthesis of polydentate ligands and their coordination complexes, whether containing homo- or hetero-donor atoms, continues to occupy a central position in coordination chemistry [8–11]. Multidentate ligands, particularly those with N_2O_2 frameworks, form highly stable metal complexes owing to the chelation effect [12]. Such structures are thermodynamically robust and are used in electronic, photonic, and nonlinear optical (NLO) applications [13,14]. Complexes of this type have also found broad use in catalysis, analytical and biomedical chemistry, photophysical and electrochemical studies, and environmental remediation [15–19]. Both symmetric and asymmetric N_2O_2 frameworks derived from Schiff bases or amine-type ligands have

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https://doi.org/10.1016/j.inoche.2025.115873
Received 28 September 2025; Received in revised form 5 November 2025; Accepted 19 November 2025