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# Preparation, spectral, X-ray powder diffraction and computational studies and genotoxic properties of new azo–azomethine metal chelates

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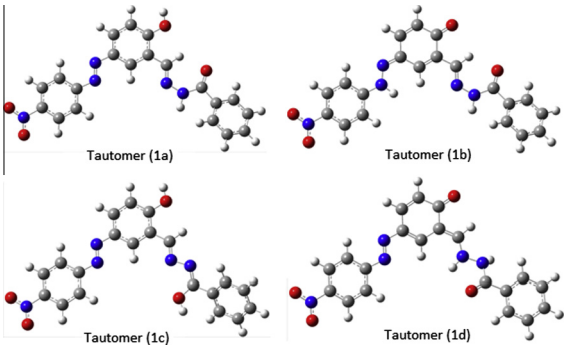
## HIGHLIGHTS

- A novel azo–azomethine ligand and its transition metal complexes were synthesized and characterized.
- The crystallinity of the azo–azomethine dye and its metal complexes were studied by X-ray powder diffraction.
- The geometrical parameters of the compounds are obtained as theoretically. The NLO properties of compounds are investigated.
- Finally, the ligand and its metal complexes are assessed for their genotoxicity.

## GRAPHICAL ABSTRACT

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## ABSTRACT

A new tridentate azo–azomethine ligand, *N′-[{2-hydroxy-5-[(4-nitrophenyl)diazenyl]phenyl}methylidene]benzohydrazidemonohydrate*, (sbH·$H_2O$) (**1**), is prepared by condensation of benzohydrazide and *2-hydroxy-5-[(4-nitrophenyl)diazenyl]benzaldehyde* (***a***) with treatment of a solution of diazonium salt of *p*-nitroaniline and 2-hydroxybenzaldehyde in EtOH. The five coordination compounds, [Co(sb)$_2$]·4$H_2O$ (***2***), [Ni(sb)$_2$]·$H_2O$ (***3***), [Cu(sb)$_2$]·4$H_2O$ (***4***), [Zn(sb)$_2$]·$H_2O$ (***5***) and [Cd(sb)$_2$]·$H_2O$ (***6***) are prepared by reacting the Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions with the ligand. The structures of the compounds are elucidated from the elemental analyses data and spectroscopic studies. It is found the ligand acts as a tridentate bending through phenolic and carbonyl oxygens and nitrogen atom of the C=N— group similar to the most of salicylaldimines. Comparison of the infrared spectra of the ligand and its metal complexes confirm that azo-Schiff base behaves as a monobasic tridentate ligand towards the central metal ion with an ONO donor sequence. Upon complexation with the ligand, the Cd(II), and Zn(II) ions form monoclinic structures, while Co(II), Cu(II) and Ni(II) ions form orthorhombic structures. Quantum chemical calculations are performed on tautomers and its metal chelates by using DFT/B3LYP method. Most stable tautomer is determined as tautomer (**1a**). The geometrical parameters of its metal chelates are obtained as theoretically. The NLO properties of tautomer (**1a**) and its metal complexes are investigated. Finally, the ligand and its metal complexes are assessed for their genotoxicity.



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## Introduction

Azo-Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions such as cobalt(II), nickel(II) and copper(II). The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species [1–3]. Schiff base ligands are well known for their wide range of applications in pharmaceutical and industrial fields [4–6]. Transition metal complexes of polydentate Schiff base ligand have great applicabilities in catalysis and material chemistry [7]. Moreover, the hydrazone group plays an important role for the antimicrobial activity and possesses interesting antibacterial, antifungal [8,9], anti-tuberculosis activities [10,11]. These groups of compounds are important class of ligands which present in numerous physiological and biological applications as antitumour agents, insecticides, anticoagulants, anticonvulsant, anti-inflammatory, analgesic, antioxidants, antiplatelet and plant growth regulators [12–16]. These properties of the hydrazones are attributed to the formation of stable metal complexes with some metals which catalyze physiological processes. Their metal complexes, have also found applications in various chemical processes like nonlinear optics, sensors, medicine [17].

Recently, azo-Schiff bases and their metal complexes were reported by our group [18–20]. In view of the versatile importance of azo–azomethines, hydrazones and their metal complexes, we herein describe the preparation and identification of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) metal complexes of *N'-[{2-hydroxy-5-[(4-nitrophenyl)diazenyl]phenyl}methylidene]benzohydrazidemonohydrate*, sbH. The chemical equations concerning the formation of the sbH ligand represented as Scheme 1. The newly synthesized azo–azomethine ligand and its metal chelates were characterized by their IR, electronic, and elemental analyses data. Finally, the ligand sbH and its Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) metal complexes were tested for their genotoxic properties.

## Experimental

### Reagents

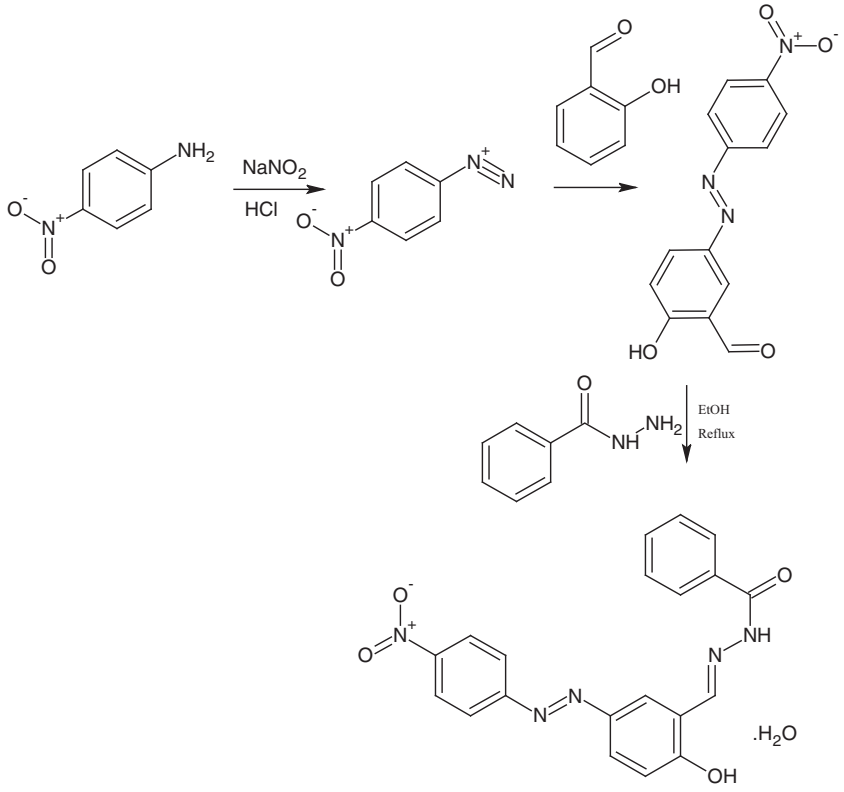
All reagents and solvents used were supplied by Merck chemical company and were used without further purification.

### Physical measurements

$^1$H NMR spectrum of the ligand was obtained in deuterated DMSO as solvent on a Bruker FT-NMR AC-400 (300 MHz) spectrometer. All chemical shifts are reported in $\delta$ (ppm) relative to the tetramethylsilane as internal standard. Carbon, hydrogen and nitrogen elemental analyses were performed with a model LECO CHNS 932 elemental analyzer. IR spectra were obtained using KBr discs (4000–400 cm$^{-1}$) on a Perkin Elmer FT-IR spectrophotometer. The UV–Vis spectra of DMSO solutions in the 200–800 nm range were measured on a T80+ UV–Vis. Spectrometer PG Instruments LTD spectrometer. X-ray powder diffraction analysis was performed by PANanalytical X'Pert PRO instrument with Cu K$\alpha$ radiation (wavelength 0.154 nm) operating at 40 kV and 30 mA. Measurements were scanned for diffraction angles ($2\theta$) ranging from 5° to 50° with a step size of 0.02° and a time per step of 1 s. Melting points were obtained with a Electrothermal LDT 9200 Apparatus in open capillaries.

### Synthesis of 2-hydroxy-5-[(4-nitrophenyl)diazenyl]benzaldehyde, (***a***)

The azo-coupled salicylaldehyde was synthesized using the known coupling methods [18]. A 1.22 g (10 mmol) of salicylaldehyde was dissolved in distilled water (30 mL) containing 0.7 g




**Scheme 1.** The synthesis reaction of *N'*-[{2-hydroxy-5-[(4-nitrophenyl)diazenyl]phenyl}methylidene]benzohydrazidemonohydrate (sbH·$H_2O$).