CRYSTAL GROWTH AND CHARACTERISATION OF NLO MATERIALS AND ITS APPLICATIONS IN VARIOUS DISCIPLINES OF BIOLOGICAL INORGANIC CHEMISTRY

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EXECUTIVE SUMMARY OF THE MINOR PROJECT TITLED CRYSTAL GROWTH AND CHARACTERISATION OF NLO MATERIALS AND ITS APPLICATIONS IN VARIOUS DISCIPLINES OF BIOLOGICAL INORGANIC CHEMISTRY

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OBJECTIVES OF THE STUDY

The main objectives of this study has been to (1) synthesize and characterize a novel ligand 9-anthraldehyde-*N*(4)-phenylsemicarbazone (NAPSC) and (2) single crystal X-ray diffraction studies of *N*(4)-phenylsemicarbazones and (3) synthesize and characterize metal complexes of *N*(4)-phenylsemicarbazones. The ligand NAPSC was characterized by elemental analyses, IR, UV-Vis, ^{1}H and ^{13}C NMR spectroscopy. Antibacterial, antifungal and cytotoxic activities of 9-anthraldehyde-*N*(4)-phenylsemicarbazone were carried out. The optimized geometry of 9-anthraldehyde-*N*(4)-phenylsemicarbazone has been calculated by

B3LYP/6-31G(d,P) level and compared with experimental data. The ligand NAPSC was screened for non-linear optical studies and found to show NLO properties. Elemental analyses data are consistent with the empirical formula of compounds. The IR spectral data of the ligands indicate that they exist in the keto form. The complexes were characterized by molar conductance, IR, UV-visible and magnetic susceptibility measurements. Single crystals of compounds of *N*(4)-phenylsemicarbazones suitable for X-ray diffraction analysis were grown from the methanol solution by slow evaporation at room temperature in air. The complexes were screened for non-linear optical studies.

SUMMARY

Interest in the field of semicarbazones stems due to their unusual coordination modes when bound to metals. Due to the high pharmacological potentialities and good chelating property of semicarbazones, the present work is mainly concentrated with the studies on ligand and complexes of N(4) substituted semicarbazones. A novel ligand 9-anthraldehyde-*N*(4)-phenylsemicarbazone (NAPSC) was synthesized in methanol solution by the condensation of 9-anthraldehyde and *N*(4)-phenylsemicarbazide in acid medium.

The ligand NAPSC was characterized by elemental analyses, IR, electronic, ^{1}H and ^{13}C NMR spectral studies. Elemental analyses data are consistent with the empirical formula of ligand. The IR data suggests that the ligand NAPSC

exist in the keto form in the solid state. This is supported by NMR spectral studies. The antimicrobial studies show that the ligand do not have any antibacterial activity towards *Escherichia coli* MTCC 585, *Salmonella typhi* MTCC 734 and *Proteus vulgaris* MTCC 1771 and do not have antifungal activity towards *Aspergillus niger* MTCC 281 and *Candida albicans* MTCC 3018. Cytotoxicity of NAPSC was determined using MTT assay against MCF-7 breast cancer cell line. The ligand shows cytotoxic activity. Low IC_{50} value of NAPSC indicates that it has higher cytotoxic activity against the tumor cell line evaluated.

Computational calculation of NAPSC was carried out with Becke's three-parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. The computations were performed at B3LYP/6-31G(d,p) levels of theory to get the optimized geometry and vibrational frequencies of the normal modes of NAPSC. The optimized geometrical parameters are in good agreement with experimental data. The computed values of the vibrational wavenumbers were compared with the values obtained from IR spectra. The difference between the corresponding wavenumbers (observed and calculated) is small, for most of the fundamental parameters. The IR activation of the C=O stretching mode shows a charge transfer interaction through a π-conjugated path. The extended π-electron delocalization over the semicarbazone moiety is responsible for the nonlinearity of the molecule. The calculated first hyperpolarizability is comparable with the reported values of similar structures,

which makes this compound an attractive object for future studies of nonlinear optics. The red shift of the NH stretching wavenumber in the infrared spectrum from the computed wavenumber indicates the weakening of the NH bond resulting in proton transfer to the neighboring oxygen atom. The ligand 9-anthraldehyde-*N*(4)-phenylsemicarbazone was screened for non-linear optical studies and found to show NLO properties.

Single crystals of compound BPSC suitable for X-ray diffraction analysis were grown from the methanol solution by slow evaporation at room temperature in air. The ligand BPSC crystallizes in a monoclinic lattice with the space group *P*2/*n*.

The complexes were characterized by molar conductance, IR, UV-visible and magnetic susceptibility measurements. The elemental analyses data are consistent with the molecular formula. The conductivity measurements were made in methanol solutions. IR spectral data show the neutral bidentate behaviour of the ligand in these complexes coordinating through the carbonyl oxygen and azomethine nitrogen. The crystal structure of Ni(II) complex of acetone-*N*(4)-phenylsemicarbazone has been determined by X-ray diffraction studies and is found that the compound crystallizes in a orthorhombic lattice with space group *P*bca. The asymmetric unit is formed by one half of the molecule and the other half is related by a centre of inversion. Bond distances within the semicarbazone ligand, particularly the C(4)–O(1) distance, which is longer than the standard C=O bond length, together with the presence of the

N–H proton, clearly indicate that the semicarbazone ligand is bound to nickel in the keto form. The complexes were screened for their non-linear optical studies using Kurtz & Perry powder technique. Experiments showed that only ligand was NLO active. This may be due to the presence of inversion centre in the crystal packing pattern of the complexes.