SYNTHESIS, CHARACTERIZATION AND STRUCTURE ELUCIDATION OF SOME SALICYLALDIMINE-BASED LIGANDS AND THEIR CORRESPONDING METAL COMPLEXES

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ABSTRACT

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A series of azo dyes were synthesized from the coupling reactions of aniline derivatives (R-C_6H_4-NH_2) (R = H, 4-CH_3, 2-Cl and 2-SO_3Na) and salicylaldehyde (C_6H_4(CHO)OH). The resulting dyes were fully characterised by several spectral and analytical methods including ^1H and ^{13}C NMR, infrared spectroscopy, electronic absorption spectroscopy, elemental analysis and single crystal studies in some cases.

The x-ray crystal structures of H_3C-C_6H_4-N=N-C_6H_3(CHO)OH (AZO1) and Cl-C_6H_4-N=N-C_6H_3(CHO)OH (AZO3) were done. For AZO1, the data showed a monoclinic crystal system and P2/c space group, with a = 21.578(5) Å, b = 4.674(5) Å, c = 11.709(5) Å, β = 95.829(5)° and volume = 1174.8(14) $Å^3$. For AZO3, the compound is also monoclinic and has a P2/n space group with a = 7.003 Å, b = 21.824 Å, c = 8.120 Å, β = 108.53° and volume = 1176.6 $Å^3$.

These dyes along with salicylaldehyde were reacted with tris(hydroxymethyl)aminomethane (Tris) via a Schiff base condensation. These were also fully characterised using several spectral and analytical methods including single crystal studies in some cases.

The single crystal x-ray structure of 2 – (hydroxymethyl) – 2- {[2-hydroxyphenyl methylidene]amino}propane-1,3–diol (Tris1) which was derived from salicylaldehyde and tris(hydroxymethyl)aminomethane showed the compound to be a monoclinic crystal system with a P2/c space group with $\beta = 101.58°$, a = 10.510(2) Å, b = 8.7270(17) Å, and c = 12.625(3) Å. Tris1 has a pK_a of 8.34, which was determined potentiometrically.

These Schiff bases were used to synthesise vanadium(V) and copper(II) complexes.

For the series of oxovanadium(V) complexes synthesized, literature and experimental data suggested the complexes are dimeric in nature with bridging alkoxo groups. These were also fully characterised. 51V NMR were carried out on these complexes. Cyclic voltammetry data suggest that in solution the complexes are monomeric with a bonded solvent molecule with a one electron transfer occurring. Detailed discussion of these complexes is presented in this work.

Animal studies were carried out on two of the vanadium(V) complex and the data showed some potential for these complexes as insulin-like drugs.

The copper(II) complexes had four copper(II) metal centres arranged as tetramer i.e. cubanes and these were also fully characterised. The x-ray diffraction studies was carried out on three of the four copper(II) complexes. Preliminary structures of **Cutr1** and **Cutr1base** were similar in nature with a monoclinic crystal system and a C2/c space group. The refinement data of $[(Cu_4(Tris2)_4)_2].3H_2O.6DMSO$ reveal the compound to be triclinic with a P-1 space group. The structure can be described as a dimer of a distorted tetramer (Cu_4O_4). A comprehensive refinement data analysis will be presented later.

Magnetic studies were carried out on the copper(II) complexes and it was observed that in all cases, between 300 to $\approx$ 65 K, the complexes behaved as four independent S = ½ spin copper ions.

Electron paramagnetic resonance (EPR) spectroscopy was carried out on all copper(II) complexes at 120 K. In all cases, the data revealed that all the valencies of the Cu(II) complexes were localised.Preliminary kinetic studies on $[(Cu_2(Tris1)_2H_2O)_2]$ (**Cutr1**) with aqueous sodium metabisulfite and *L*-ascorbic acid revealed that both reactions are proceed via similar mechanisms , which consisted of two separate steps.