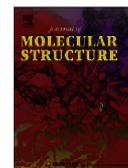


## Research Publications

1. Rahul Kadu, Vinay K Singh,\* **Sanjay K Verma**, “Pallepogu Raghavaiah and Mobin M Shaikh, Effect of substituents on crystal packing of functionalized 4,4'-bis(benzylideneamino)diphenyl ether(s) and their reduced benzyl forms: Synthesis, characterization, optical and thermal properties” *J. Mol. Struct.*, 1033 (2013) 298–311.
2. **Sanjay K. Verma**, Rahul Kadu and Vinay K. Singh,\* “A Facile Synthesis, Crystallographic, Spectral, Thermal and Electrochemical Investigations of Neutral  $[\text{Cu}_2(\text{Et}_2\text{dtc})_4]$  Dimer” *Synth. React. Inorg. Met-Org. Nano-Metal Chem.*, 44 (2014) 441–448.
3. **Sanjay K. Verma** and Vinay K. Singh,\* “One pot three component synthesis of mononuclear  $[\text{M}(1,1\text{-dithiolato})_2]$  {Mn(II), Co(II), Zn(II) and Cd(II)} complexes, spectral characterization, fluorescence, optical and thermogravimetric study” *Polyhedron* 76 (2014) 1-9.
4. **Sanjay K. Verma** and Vinay K. Singh,\* “[ $\text{M}\{\kappa^2\text{S},\text{S}-\text{S}_2\text{C-piperazine-C}_2\text{H}_4\text{N}=\text{C}(\text{R})\}_n$ ] {Co(III), Ni(II), Cu(II) or Zn(II)} complexes bearing pendant Schiff base moieties: spectral characterization, fluorescence, cyclic voltammetric and TGA/DTA study” *J. Coord. Chem.* 68 (2015) 1072–1087.
5. Vinay K Singh,\* **Sanjay K Verma**, Rahul Kadu and Shaikh M. Mobin, “Identification of unusual C–Cl... $\pi$  contacts in 2-(alkylamino)-3-chloro-1,4-naphthoquinones: Effect of *N*-substituents on crystal packings, fluorescence, redox and anti-microbial properties” *RSC Advances* 5 (2015) 43669–43686.
6. **Sanjay K. Verma** and Vinay K. Singh,\* “Synthesis and characterization of ferrocene functionalized transition metal dithiocarbamate complexes: Investigations of antimicrobial, electrochemical properties and a new polymorphic form of  $[\text{Cu}\{\kappa^2\text{S},\text{S}-\text{S}_2\text{CN}(\text{CH}_2\text{C}_4\text{H}_3\text{O})\text{CH}_2\text{Fc}\}_2]$ ” *J. Organomet. Chem.* 791 (2015) 214–224.
7. **Sanjay K. Verma** and Vinay K. Singh,\* “Synthesis, electrochemical, fluorescence and antimicrobial studies of 2-chloro-3-amino-1,4-naphthoquinone bearing mononuclear transition metal dithiocarbamate complexes  $[\text{M}\{\kappa^2\text{S},\text{S}-\text{S}_2\text{C-piperazine-C}_2\text{H}_4\text{N}(\text{H})\text{CINQ}\}_n]$ ” *RSC Advances*, 5 (2015) 53036-53046.



## Effect of substituents on crystal packing of functionalized 4,4'-bis(benzylideneamino)diphenyl ether(s) and their reduced benzyl forms: Synthesis, characterization, optical and thermal properties

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### ABSTRACT

In this paper we report the synthesis of 4,4'-bis(benzylideneamino)diphenyl ether (1), 4,4'-bis(*p*-methoxybenzylideneamino)diphenyl ether (2), 4,4'-bis(*p*-nitrobenzylideneamino)diphenyl ether (3), 4,4'-bis(benzylamino)diphenyl ether (4) and 4,4'-bis(*p*-methoxybenzylamino)diphenyl ether (5). The new compounds were characterized by using standard spectroscopic techniques. Supramolecular structures of 1–4 have been studied by using single-crystal X-ray diffraction to gauge the influence of substituents, present on *para*-positions of peripheral phenyl rings, on the association of molecules in the solid state. The study showed that introduction of *p*-OCH<sub>3</sub> and *p*-NO<sub>2</sub> substituents on peripheral phenyl rings, successfully switches off CH···π synthons seen in compound 1 and 4 and that the new compounds adopt other packing strategies based on CH···O (2) and CH···N, CH···O and π···π (3) interactions. The optical band gaps (*E*<sub>g</sub>), calculated by optical absorption method fall in the range of 2.16–3.0 eV and demonstrate a wide band gap semiconducting nature of these compounds. The thermogravimetric study of these compounds suggests the total destruction of the molecules up to 550 °C with a remaining mass of <10%, except the 3.

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### 1. Introduction

The existence of C—H···O hydrogen bond, which was initially suggested by Glasstone in 1937 [1] and later on by Sutor in early 1960s [2,3], is now well established in the structural chemistry. Several investigations, especially on C—H···O [4] and C—H···N [5] containing C—H groups as donor groups, have been carried out. The significance of these interactions along with weak C—H···π [6] and π···π [7] interactions as a directing tool in the organization of molecules has been recognized in both chemistry and biology and thus implicated successfully in the crystal engineering [8] and supramolecular assemblies [9]. Understanding of the molecular packing is important because of material properties, often governed by the way in which their constituent molecules are arranged [10]. That knowledge is further imperative in crystal engineering and structural chemistry to deliberately engineer the arrangement of molecules in new materials. However, predetermination of molecular packing is a big challenge to the researchers, as intermolecular forces that hold the molecules in the solid state are inadequately understood and hard to predict, particularly for

organic solids [11]. Thus any step taken into predictable molecular packing is a practical movement towards the ultimate goal of structural chemistry to design new solid of desired properties.

Supramolecular structures of several organic molecules and their properties are clearly shown to be sustained *via* hydrogen bonds and π···π interactions. For instance, a clear analogy between the structures and polymorphs of methoxy-substituted distyrylpyrazines has been emerging from a detailed comparison of their supramolecular structures stabilized *via* C—H···O, π···π and C—H···N interactions [12]. It is clear that favorable non-covalent interactions between organic molecules include π···π and C—H···π interactions, nevertheless, both types of interactions appeared to be a subject of the electronic nature of substituents [13]. Furthermore, it has been demonstrated in the literature that helicity in the supramolecular architecture can be induced by conformational limits of macromolecules, inter-, intra-molecular hydrogen bonds or coordination to metal ions. A majority of helical molecular assemblies in the crystalline phase reported to date have been constructed by the use of achiral building blocks [14].

Apart from this, plenty of efforts have been made in the synthesis and isolation of novel imines (>C=N—) since the first report in 1864 by Hugo Schiff. This is mainly because of their potential utilities in various fields such as synthetic, structural, medicinal and

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# A Facile Synthesis, Crystallographic, Spectral, Thermal, and Electrochemical Investigations of Neutral [Cu<sub>2</sub>(Et<sub>2</sub>dtc)<sub>4</sub>] Dimer

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A neutral dimeric complex [Cu<sub>2</sub>(Et<sub>2</sub>dtc)<sub>4</sub>] (dte = dithiocarbamate) (1) was synthesized in single step under mild conditions. Structure of 1 has been studied using single-crystal XRD to gauge the influence of CH<sub>3</sub> and CH<sub>2</sub> groups of coordinated dithiocarbamate ligands on the association of the molecules in solid state. Evidently 1 features the ability of these groups to form intermolecular (sp<sup>3</sup>)C–H···π(chelate ring) and (sp<sup>3</sup>)C–H···S stacking interactions leading to fascinating 3D infinite network. Complex has been completely characterized by spectrophotometric methods, optical behavior, and thermal and cyclic voltammetry studies. Cyclic voltammetric study confirmed the binding affinity of 1 toward H<sub>2</sub>PO<sub>4</sub><sup>−</sup>.

Supplemental materials are available for this article. Go to the publisher's online edition of Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry to view the supplemental file.

**Keywords** cyclic voltammetric study, fluorescence, optical band gap, (sp<sup>3</sup>)C–H···π(chelate ring) interaction, (sp<sup>3</sup>)C–H···S interaction, TGA/DTA, UV-visible

## INTRODUCTION

There is a growing interest in identifying the nature of non-conventional intermolecular interactions,<sup>[1]</sup> because of their increasing demand in the situations where conventional hydrogen bonding does not extend in three dimensions or does not exist due to lack of appropriate donors and acceptors. Interactions of the type C–H···O,<sup>[2]</sup> C–H···π,<sup>[3–5]</sup> and π···π,<sup>[6]</sup> are well established in the crystal engineering where the hydrogen

atoms associated with the aromatic moieties are generally more amenable for C–H···π interactions than the hydrogen atoms associated with a sp<sup>3</sup> carbon atoms.<sup>[5]</sup> However, a recent investigation<sup>[4]</sup> showed that the directionality and strength of interactions involving (sp<sup>3</sup>)C–H group are more significant in terms of the access angle and the shorter distance between the hydrogen atom and acceptor. The existence of C–H···S interactions is less common<sup>[7]</sup> than C–H···O interactions but may be found in many molecular crystals with fascinating properties such as electrical conductivity or superconductivity.<sup>[8]</sup> Recently, metal-chelate rings of suitable 1,1-dithiolate metal complexes were reported to act as C–H acceptors. Thus certain complexes were apparently sustained by C–H···π(chelate ring) interactions.<sup>[9]</sup> Since “metalloaromaticity” was discovered in 1945,<sup>[10]</sup> a large number of transition metal chelate rings feature this metalloaromaticity.<sup>[11]</sup> However, the existence of C–H···π(chelate ring) interaction in both coordination and organometallic compounds is very limited and definition of structural parameters for such interactions to occur is still being explored. The hydrogen bond energy for C–H···π(chelate ring) interactions, 6–11 kJ mol<sup>−1</sup>,<sup>[12]</sup> was found to be comparable with C–H···π(organic) interactions, 1–8 kJ mol<sup>−1</sup>.<sup>[13]</sup> Thus the reliability on the C–H···π(chelate ring) synthons certainly provides a new directing tool of molecular assembly for coordination and organo-metallic compounds.

On the other hand, metal complexes with sulfur rich ligands are very interesting due to their involvement in the growth of thin layers of metal sulfides, by metal-organic chemical vapor deposition techniques, electrochemical properties, electrical properties, and biological properties. In particular, the introduction of metal dithiocarbamate complexes bearing a direct metal-sulfur bond, as a single source precursor, has proven to be a very efficient and an alternative route for the synthesis of high-quality semiconductor nanoparticles.<sup>[14]</sup> Alternatively, the metal dithiocarbamate complexes have been employed as anion binding motifs.<sup>[15]</sup>

Although the structural investigations on copper(II) bis(*N,N*-diethyldithiocarbamate) complex were previously made by Bonamico<sup>[16]</sup> and Jian's research group,<sup>[17]</sup> however, we report herein an efficient single-step synthesis of copper(II) bis(*N,N*-diethyldithiocarbamate) complex dimer [Cu<sub>2</sub>(Et<sub>2</sub>dtc)<sub>4</sub>] 1, which

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# One pot three component synthesis of mononuclear $[M(1,1\text{-dithiolato})_2]$ $\{Mn(II), Co(II), Zn(II) \text{ and } Cd(II)\}$ complexes, spectral characterization, fluorescence, optical and thermogravimetric study



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## ABSTRACT

A series of neutral monometallic bis-dithiocarbamate complexes,  $[M(1,1\text{-dithiolato})_2]$   $\{1,1\text{-dithiolato} = 3\text{-dithiocarbamato coumarin}; M = Mn(II) \text{ 1, } Co(II) \text{ 2, } Zn(II) \text{ 3 and } Cd(II) \text{ 4}\}$ , was efficiently synthesized in a single pot reaction using 3-amino coumarin,  $CS_2$  and  $M(OAc)_2$ . All the complexes were characterized by microanalysis, ESI MS, FT-IR,  $^1H$  and  $^{13}C$  NMR, UV-Vis absorption, fluorescence, magnetic susceptibility and thermogravimetric studies. Evidently the 3-dithiocarbamato coumarin ligand behaves as monobasic bidentate in all the complexes. The electronic absorption and magnetic moment data support a distorted tetrahedral geometry around Mn(II) and a rare low spin square planar geometry around Co(II), as well as square planar Zn(II) and Cd(II) centres. The fluorescence spectra of all complexes exhibit concomitant bathochromic shifts of the intra-molecular (CT  $\rightarrow$  M) charge-transfer emissions. Interestingly, the thermal decomposition of complexes 2–4 gave a metal sulfide as the final product and this indicates that these complexes may provide a single source material for the preparation of metal sulfide nanoparticles. The calculated band gap energies ( $E_g$ ) fall in the range 2.039–2.565 eV, suggesting the feature of a direct band gap semiconducting nature for complexes 1–4.

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## 1. Introduction

Interest in the chemistry of metal complexes containing sulfur rich ligands has been continued because of their wide applications in the area of electrical conductivity, molecular magnetism, electrochemical and biological processes, and optoelectronic properties [1]. In particular, the use of polydentate dithiocarbamate ligands has emerged as one of the most active areas of research in chemistry due to their versatile coordination chemistry, material properties and industrial applications [2]. They are ideal candidates to use extensively in separation techniques [3] due to their ability to form stable chelates with a number of metal ions. They have also been used in medicine due to the existence of the dithiocarbamate moiety in a variety of biologically active molecules [4].

Apart from this, dithiocarbamate complexes, with a direct metal-sulfur bond, as a single source precursor have proven to give a very efficient and an alternative route for the synthesis of high-quality semi-conductor nanoparticles [5]. It appears that many of these complexes are used for the production of lead, cadmium, zinc, mercury and copper sulfides [6].

Thermogravimetric studies of metal dithiocarbamate complexes suggest their wide spread use for industrial applications, such as in foam rubber, fungicides, effective heat stabilizers, antioxidant action, reprocessing of polymers etc. [7]. It further suggests the suitability of complexes to be used as single source precursors for the synthesis of metal sulfide nanoparticles and thin films [8]. It has been found that the size and shape of the metal sulfide nanoparticles greatly depend on the nature of the organic moiety present in the metal dithiocarbamate complexes [9], which consecutively affect fundamental attributes such as optical, electrical and mechanical properties [10].

Although a wide range of biological activities, including CNS depressant, antibacterial, antiallergic and insect-growth regulatory effects have been shown by the derivatives of 3-amino coumarin [11], together with antimicrobial and antioxidant activities by their transition metal complexes [12], no attempt has been made so far to investigate the synthesis, stability, structure and reactivity of dithiocarbamate derivatives of 3-amino coumarin. In the present work we have demonstrated the one pot synthesis of a novel series of  $[M(1,1\text{-dithiolato})_2]$   $\{1,1\text{-dithiolato} = 3\text{-dithiocarbamato coumarin}; Mn(II) \text{ 1, } Co(II) \text{ 2, } Zn(II) \text{ 3 and } Cd(II) \text{ 4}\}$  complexes. These complexes have been thoroughly characterized by microanalysis, ESI MS, FT-IR,  $^1H$  and  $^{13}C$  NMR, UV-Vis absorption, magnetic

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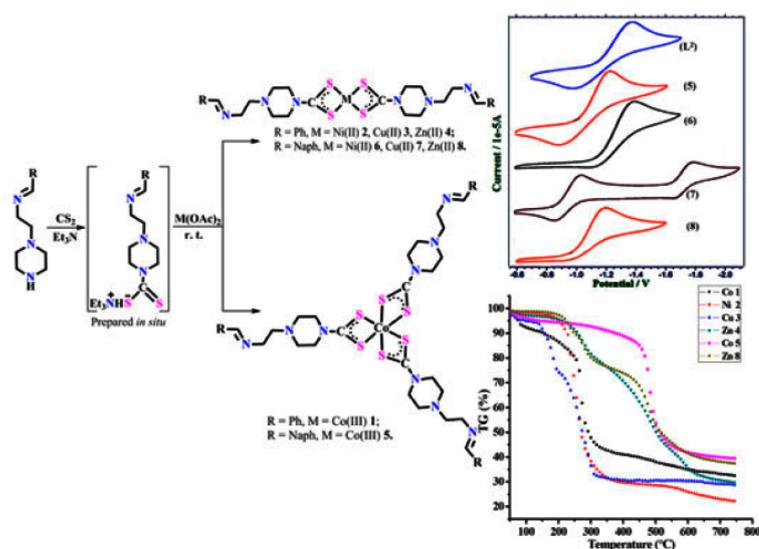
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## $[M\{\kappa^2S,S-S_2C\text{-piperazine-C}_2\text{H}_4\text{N}=\text{C}(\text{R})\}_n]$ {Co(III), Ni(II), Cu(II) or Zn(II)} complexes bearing pendant Schiff base moieties: spectral characterization, fluorescence, cyclic voltammetric and TGA/DTA study

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A series of neutral mononuclear complexes  $[M\{\kappa^2S,S-S_2C\text{-piperazine-C}_2\text{H}_4\text{N}=\text{C}(\text{R})\}_n]$  {R = Ph; M = Co(III) 1, Ni(II) 2, Cu(II) 3, Zn(II) 4; R = Naph; M = Co(III) 5, Ni(II) 6, Cu(II) 7, Zn(II) 8;  $n = 2$  for 2–4, 6–8 and  $n = 3$  for 1, 5} bearing pendant Schiff base moieties were synthesized through self-assembly involving N-[phenylmethanimine]-2-piperazin-1-ylethanamine (L<sup>1</sup>) or N-[naphthylmethanimine]-2-piperazin-1-ylethanamine (L<sup>2</sup>) with two equivalents each of CS<sub>2</sub> and corresponding metal acetates. The complexes 1–8 were characterized by microanalysis, ESI-MS, IR, <sup>1</sup>H, <sup>13</sup>C NMR, DEPT 135, UV–visible absorption, and emission spectroscopy. Complexes 1, 3, and 8 exhibit fluorescence emissions at 342, 344, and 348 nm upon excitation at 273 (for 1 and 3) and 263 (for 8) with concomitant Stokes shifts of 69, 71, and 85 nm. The spectral and magnetic moment data support octahedral geometry around Co(III) and square planar/tetrahedral geometry around other metal centers. Thermal stabilities of 1–8 have been investigated by thermogravimetric analysis. The cyclic voltammograms clearly suggest that the complexes exhibit electroreduction principally associated with pendant imine moieties except Cu(II) complex 7 which displays quasi-reversible reduction

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## Identification of unusual C–Cl $\cdots$ $\pi$ contacts in 2-(alkylamino)-3-chloro-1,4-naphthoquinones: effect of N-substituents on crystal packing, fluorescence, redox and anti-microbial properties†

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The chemo-selective reaction of 2,3-dichloro-1,4-naphthoquinone with different primary amines affords access to a series of derivatives, such as 2-(alkylamino)-3-chloro-1,4-naphthoquinone (1–6) and 2-(benzylamino)-1,4-naphthoquinone (7), in good yields. All the compounds 1–7 were characterized thoroughly by microanalysis, standard spectroscopy and thermogravimetric methods. The supramolecular structures of 1–4 and 7 were studied by means of single-crystal X-ray diffraction to gauge the influence of substituents that are present on the amine functionality on the association of molecules in the solid state. The study showed that the introduction of various amine N-substituents induces conformational changes that apparently modify the nature and number of donor–acceptor sites for noncovalent interactions, leading to diverse crystal packing patterns. Interestingly, the introduction of 2-(benzylamino)- and 2-(2-pyridylmethylamino)- substituents in 2 and 4 successfully switched on the C–Cl $\cdots$  $\pi$  synthon, which is scarcely seen in the crystal packing of organic molecules. Compounds 1, 2, 4 and 5 fluoresced in the range of 350–620 nm with concomitant Stokes shifts of 81, 131, 141 and 131 nm, respectively, and their cyclic voltammograms evidenced two quasi-reversible single-electron waves. All the compounds (except 5) exhibited their first endothermic peak on the DTA curves without any mass loss due to the phase change, attributable to the melting points of the respective compounds. Remarkably, compound 5 exhibited an enhanced antibacterial activity against *S. aureus* and proved to be a more potent antibacterial agent than the well-known drug “ciprofloxacin”.

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### 1. Introduction

The intermolecular forces that hold the molecules in the solid state are inadequately understood and hard to predict, particularly for organic solids.<sup>1</sup> Because the properties of a material are often governed by the way in which its constituent molecules are arranged,<sup>2</sup> any step taken into predicting molecular packing is a practical movement towards the ultimate goal of structural chemistry to design new solids with desired properties. Hydrogen bonds and stacking interactions, including weak hydrogen bonds such as C–H $\cdots$ O,<sup>3</sup> N–H $\cdots$ O,<sup>4</sup> C–H $\cdots$  $\pi$ <sup>5</sup> and  $\pi$  $\cdots$  $\pi$ <sup>6</sup> interactions, are considered as the main directing tools in the organization of molecules in both chemistry as well as in

biology. These have been implicated successfully in both the crystal engineering and supramolecular assemblies. However, the ability of halogen atoms to function as reliable sites for directing intermolecular recognition processes was largely overlooked until the 1990s. Halogen bonds have been recognized recently as another type of non-covalent interaction that can be used as a new tool for the organization of supramolecular systems and molecular crystals.<sup>7</sup> They have been shown to be accountable for the formation of a variety of stable supramolecular assemblies in crystals,<sup>7,8</sup> biological systems,<sup>9</sup> solutions,<sup>10</sup> and even in the gas phase.<sup>11</sup> A competition between hydrogen bonding and halogen bonding has been observed by Professor Aakeroy's group and others<sup>12</sup> during the supramolecular assembly of organic molecules in the solid state. More interestingly, rational modifications of the hierarchy of intermolecular interactions in molecular crystal structures using tuneable halogen bonds have been developed.<sup>13</sup> In particular, halogen bonds of the type C–H $\cdots$ Cl<sup>7b,14</sup> have been investigated significantly; however, literature shows only a few reports<sup>8,15</sup> on the existence of C–Cl $\cdots$  $\pi$  interactions. A survey of the protein data bank (PDB) suggested only a limited number of C–Cl $\cdots$  $\pi$  interactions have been retrieved from crystal structures of

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† Electronic supplementary information (ESI) available: Additional figures and CIF files. See CCDC reference numbers 986339 for 1; 986337 for 2; 986340 for 3; 986336 for 4 and 986338 for 7. CCDC 986336–986340. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra02295a



## Synthesis and characterization of ferrocene functionalized transition metal dithiocarbamate complexes: Investigations of antimicrobial, electrochemical properties and a new polymorphic form of $[\text{Cu}\{\kappa^2\text{S}_2\text{S}-\text{S}_2\text{CN}(\text{CH}_2\text{C}_4\text{H}_3\text{O})\text{CH}_2\text{Fc}\}_2]$



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### ABSTRACT

A straightforward single pot reaction of *N*-methylaryl-*N*-methylferrocenyl amine ( $\text{L}^1\text{-L}^3$ ),  $\text{CS}_2$  and  $\text{M}(\text{OAc})_2$  in  $\text{Et}_3\text{N}$  at room temperature led to the formation of  $[\text{M}\{\kappa^2\text{S}_2\text{S}-\text{S}_2\text{CN}(\text{CH}_2\text{R})\text{CH}_2\text{Fc}\}_n]$  ( $\text{M} = \text{Co}^{\text{III}}$ ,  $\text{R} = 1\text{-naphthyl}$ , (1), 3-pyridyl (2), 2-furyl (3);  $\text{M} = \text{Ni}^{\text{II}}$ ,  $\text{R} = 1\text{-naphthyl}$ , (4), 3-pyridyl (5), 2-furyl (6);  $\text{M} = \text{Cu}^{\text{II}}$ ,  $\text{R} = 1\text{-naphthyl}$ , (7), 2-furyl (8);  $\text{M} = \text{Zn}^{\text{II}}$ ,  $\text{R} = 1\text{-naphthyl}$ , (9);  $n = 3$  for 1–3 and  $n = 2$  for 4–9).  $\text{L}^1\text{-L}^3$  and 1–9 were characterized by microanalysis and standard spectroscopic methods viz. MS, IR,  $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT 135 NMR, UV–vis. absorption and emission spectroscopy. Single crystal X-ray diffraction technique was used to detect a new polymorphic form of 8, sustained by significant  $\text{S}/\text{lp}\cdots\pi$  and  $\text{C}-\text{H}\cdots\pi$  intermolecular interactions. All the compounds were screened against a panel of microbes viz. *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Candida albicans* and *Aspergillus niger*. Remarkably,  $\text{L}^1$ , 4 and 8 were found to have better antibacterial activity against *S. aureus* than Ciprofloxacin, while compound 5 was found to be as good an antifungal agent as Flucanazole against *C. albicans*. All the compounds display a single quasi-reversible cyclic voltammograms and formal redox potentials in the range of 407 to 224 mV vs  $\text{Ag}/\text{Ag}^+$  ( $\text{CH}_3\text{CN}$ ).

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### Introduction

Since the discovery of ferrocene [1] there is a substantial growth in the chemistry utilizing the ferrocene [2,3] typically because of its lipophilic character, ease of chemical modification and accessible one-electron-oxidation potential. In spite of the nontoxic nature of ferrocene, its stability in aqueous and aerobic media and biological inertness, many ferrocenyl derivatives exhibit significant anticancer, antibacterial, antiparasitic, antifungal, and other biological activities [4]. Thus it has appeared at the forefront of bio-organometallic chemistry. The biological activity of these derivatives is reportedly associated with the attachment of the ferrocenyl group to either biologically relevant molecules or with the molecules that do not exhibit biological activity on their own. Potential examples include ferrocenyl analogues of tamoxifen [5] and the antiparasite ferroquine derivatives [6] where ferrocenyl

fragment efficiently potentiate the biological activity of the conjugated pharmacophore. Edward's research group has synthesized a series of antibiotics containing ferrocene moiety such as ferrocenyl penicillin, ferrocenyl cephalosporine and ferrocenyl hybrid of penicillin and cephalosporine [7].

On the other hand, metal complexes with sulphur-rich ligands are very interesting from the viewpoint of their electrical conductivity, molecular magnetism, electrochemistry, optoelectronic properties and biological processes [8,9]. In particular, dithiocarbamate has drawn a lot of attention since its first derivative tetramethylthiuram disulfide, generally known as thiram has achieved prominence fungicidal properties [10]. Compounds having dithiocarbamate (DTC) groups, were proven medicinally significant and utilized as microbicidal spermicides [11], anesthetic [12], anti-HIV [13], mono glyceride lipase inhibitors [14], anti-tumour agents [15]. The unique redox property of the sulphur atom in DTC make it as a key residue for enzyme catalysis, protein folding and redox signalling [16]. These are important processes required for cellular energy metabolism, motility and subsistence of cellular systems. These properties of the DTC bring about a versatile pharmacophore

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## Synthesis, electrochemical, fluorescence and antimicrobial studies of 2-chloro-3-amino-1,4-naphthoquinone bearing mononuclear transition metal dithiocarbamate complexes $[M\{\kappa^2S,S-S_2C\text{-piperazine-C}_2\text{H}_4\text{N(H)CINQ}\}_n]^\dagger$

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A novel multifunctional ligand precursor 2-chloro-3-(2-(piperazinyl)ethyl)-amino-1,4-naphthoquinone (L) was synthesized by chemo-selective reaction of 2,3-dichloro-1,4-naphthoquinone and 2-(piperazin-1-yl)ethanamine and characterized, prior to use. A series of mononuclear transition metal dithiocarbamate complexes  $[M\{\kappa^2S,S-S_2C\text{-piperazine-C}_2\text{H}_4\text{N(H)CINQ}\}_n]$  ( $M = \text{Mn(III)}$  1,  $\text{Co(II)}$  2,  $\text{Ni(II)}$  3,  $\text{Cu(II)}$  4,  $\text{Zn(II)}$  5;  $\text{CINQ} = 2\text{-chloro-1,4-naphthoquinone}$ ;  $n = 3$  for 1–2 and  $n = 2$  for 3–5) bearing pendant 2-chloro-3-amino-1,4-naphthoquinone groups were efficiently synthesized through a self-assembly process involving L,  $\text{CS}_2$  and corresponding metal acetates. 1–5 were characterized by microanalysis and standard spectroscopic methods such as ESI-MS, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and UV-visible absorption spectroscopy. Significantly, all compounds exhibit medium to very strong fluorescence emission bands in the visible region with concomitant Stokes shifts of  $\approx 280$  nm upon excitation at their respective  $\lambda_{\text{max}}$  values. Thermal stability of complexes 1–5 has been investigated by thermogravimetric analysis. Cyclic voltammetric study clearly reveals that L and 1–5 are electro active with respect to the dominant redox-active naphthoquinone moiety. Further, L and 1–5 were tested against six important pathogen microorganisms viz. *S. aureus*, *B. subtilis*, *E. coli*, *P. aeruginosa*, *C. albicans* and *A. niger* by using the Broth dilution method. A broad spectrum of the strongest antimicrobial activity was determined for the copper(II) complex 4 and L. The enhanced antibacterial activity of L and copper(II) complex 4 against *S. aureus* apparently reveals them to be a superior antibacterial agent than the reference drug ciprofloxacin.

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### 1. Introduction

Over the decades, transition metal complexes derived from sulphur rich ligands have received a great deal of attention because of their conducting properties, molecular magnetism, electrochemical, optoelectronic properties and biological applications.<sup>1–8</sup> In particular, dithiocarbamates have emerged as versatile ligands to construct a huge variety of inorganic–organic complex materials with fascinating physico-chemical properties. The ease of synthesis and ability to bind to a wide range of elements in different oxidation states<sup>9–11</sup> add further merit to this ligand system. The dithiocarbamate group is considered as a versatile pharmacophore since the discovery of the first dithiocarbamate derivative *i.e.*

tetramethylthiuram disulfide (thiram),<sup>12</sup> which has prominent fungicidal properties and hence, it is used in compounds of biological interest.<sup>13</sup> Thermogravimetric studies have been utilized to demonstrate the widespread industrial applications of dithiocarbamate compounds such as foam rubber, fungicides, effective heat stabilizers, suitability as a single source precursor for the preparation of metal sulphide nano-particles, antioxidant action, reprocessing of polymers *etc.*<sup>14</sup>

On the other hand, considerable attention has been paid to the functionalization of naphthoquinone derivatives and evaluation of their biological properties, mainly due to their association with multiple biological oxidative processes.<sup>15</sup> Literature reports suggest that naphthoquinone derivatives possess a wide range of biological properties that include antibacterial and antifungal, antiviral, antimalarial and anticancer activity which have stimulated the study of these bioactive compounds in the field of medicinal chemistry.<sup>16</sup> However, we could not find even a single report on the dithiocarbamate derivatives of naphthoquinone and their transition metal complexes. Although, an

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### **Papers presented in the International Conferences:**

1. **Sanjay K. Verma**, Vinay K Singh and Shaikh M. Mobin. Synthesis and Antimicrobial Studies of Metal dithiocarbamate Complexes Derived From 2-Amino-3-Chloro-1,4-Naphthoquinone. International Conference on Innovations in Chemistry For Sustainable Development (ICSD-2011), Punjab University, Chandigarh, December 01-03, 2011.
2. **Sanjay K. Verma** and Vinay K. Singh. Luminescent Mononuclear Bis-*S,S*-bidentate Complexes Derived from 3-Aminocoumarin: Synthesis, Spectral and Thermogravimetric Study. International Conference on Chemistry and Materials: prospects and Perspectives-2012, Babasaheb Bhimrao Ambedkar University (A Central University) Vidya Vihar, Raibareli Road Lucknow- 226 025, (India) December 14-16, 2012.
3. **Sanjay K. Verma** and Vinay K. Singh. Luminescent Monometallic Bis-1,1-dithiolato Complexes Derived from 3-Aminocoumarin: Synthesis, Spectral, Optical and TGA/DTA Study. International Conference on Science and Engineering on Materials (ICSEM-2014) School of Engineering and Technology Sharda University Greater Noida, India, 6-8 January 2014.

### **Papers presented in the National Conferences:**

1. **Sanjay K. Verma** and Vinay K. Singh. Mononuclear Metal Complexes  $M(dtc)_2$  (*dtc* = dithiocarbamate) Bearing Coumarin moiety: Synthesis, Characterization and Thermal Gravimetric Study. Western India Research Scholars's Meet 2011 (WIRSM-2011), Department of Chemistry, M. S. U, Baroda, September 17, 2011.
2. Vinay K. Singh, **Sanjay K. Verma**, Rahul Kadu and Shaikh M. Mobin. Complexes Based on Coumarin Schiff Bases: Synthesis, Characterization and Anti-Bacterial Studies. Modern Trends in Inorganic Chemistry (MTIC-XIV), School of Chemistry, University of Hyderabad, December 10-13, 2011.
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5. **Sanjay K. Verma**, Rahul Kadu, Vinay K Singh and Shaikh M. Mobin. Novel Organic Precursors for the Development of Monometallic DTC Complexes. National Symposium on Modern Trends in Chemistry (MTC-2013) Department of Chemistry, faculty of Science, M. S. U, Baroda, March 21-23, 2013.