❖ List of papers published

1. **Synthesis, X-ray crystallographic, Hirshfeld, DFT study and interactions with TNFα receptors of chiral bisimines and diamines holding thiophene spacers,** Komal Kolte, Shailykumari K. Patel, Vinay K. Singh, Journal of Molecular Structure **2023** 1300 137165.
2. **Macrocyclic Ni^{II}-Xanthate $[Ni^{II}_2\text{-}\mu^2\text{-bis-}\{(\kappa^2 S,S\text{-}S_2COCH_2CH_2)_2N(Ts)\}]$ Complex and a Cyclic Thiocarbonate Monomer: Synthesis, Crystallography, Photophysical, TD-DFT and Investigation of Thermochromism**, Rahul Kadu, Komal Kolte, Chirag Savani, Sanjio S. Zade, Anvarhusein A. Isab, Atresh Kumar Singh, Vinay K. Singh, Journal of Molecular Structure **2023** 1287 135657.
3. **New series of M^{II}-dithiocarbamate complexes ($M = Cu^{II}$, Ni^{II} and Zn^{II}) holding pendant *N,O*-Schiff base moieties: Synthesis, characterization, photophysical, crystallographic, anti-microbial and DFT study**, Shailykumari K. Patel, Komal Kolte, Chirag J. Savani, Pallepogu Raghavaiah, Dhruti Dave, Anvarhusein A. Isab, Disha Mistry, Devesh Suthar, Vinay K. Singh, Inorganica Chimica Acta **2022** 543 121139.

❖ List of papers under communication

1. ***N,N'*-bis(3-dithiocarbamatopropyl) piperazine bridged metallomacrocyclic complexes of Ni(II), Cu(II) and Zn(II): synthesis, characterization, photophysical, in-silic o study and their potential utility in heavy metal ion sensing,** Komal Kolte, Alka Singla, Arun Kumar Das, Vinay K. Singh **(Under review in Inorganic Chemistry)**
2. **Employment of novel Binuclear Metallomacrocyclic Dithiocarbamate Hosts of Ni^{II}, Cu^{II} and Zn^{II} for Selective binding with Environmentally Hazardous Dyes: Synthesis, Characterization and in- Silico Study,** Komal Kolte, Priyanka Mathur, Arpita Desai, Vinay K. Singh **(Under Communication)**
3. **Synthesis, characterization and metal ion sensing study of novel Metallomacrocylcic dithiocarbamate complexes holding thiophenyl groups in the macrocyclic framework,** Komal Kolte and Vinay Kumar Singh **(Under Manuscript Preparation)**

Journal of Molecular Structure 1300 (2024) 137165

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Synthesis, X-ray crystallographic, Hirshfeld, DFT study and interactions with TNFα receptors of chiral bisimines and diamines holding thiophene spacers

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ARTICLE INFO

Keywords:
Chiral bisimines
Chiral diamines
Single crystal XRD
Hirshfeld
DFT
TNFα

ABSTRACT

This paper outlines a facile synthesis of chiral bisimines *R,R*-(Thiophene-2,5-diyl)bis(N-(1-phenylethyl)methanimine) *R,R*-**BI-1**, *S,S*-(Thiophene-2,5-diyl)bis(N-(1-phenylethyl)methanimine) *S,S*-**BI-2** and their reduced products R,R-(Thiophene-2,5-diyl)bis(N-(1-phenylethyl)methanamine) *R,R*-**DA-1**, S,S-(Thiophene-2,5-diyl)bis (N-(1-phenylethyl) methanamine) *S,S*-**DA-2** holding thiophene spacers. The new derivatives were suitably characterized by microanalysis, standard spectroscopic techniques (^{1}H, ^{13}C NMR, FTIR, UV–visible absorption). Single crystal X-ray diffraction (SCXRD) method was used to study the supramolecular structures of *R,R*-**BI-1** and *S,S*-**BI-2**, sustained primarily by C—H…π intermolecular contacts which are well supported by molecular electrostatic potential (MESP). Quantification of short contacts existing in the crystal packing of these molecules was accomplished by Hirshfeld surface and fingerprint plots calculations. The geometry of all the molecules has been optimized by using a density functional theory calculation and the theoretical data were compared well with the experimental outcomes. Further, the calculated HOMO-LUMO band gaps for *R,R*-**BI-1**, *S,S*-**BI-2**, *R,R*-**DA-1** and *S,S*-**DA-2** (4.05–5.30 eV) suggests their non-conducting nature. Moreover, virtual screening of these nitrogenous compounds has been performed by molecular docking study to propose their potentials as biologically relevant molecules.

1. Introduction

There is growing research in the development of novel imines and amines [1] due to their prevalent applications in research laboratories and industries for the synthesis of fine chemicals used ubiquitously in biology, dyes, agrochemicals, surfactants and lubricants [2]. In particular, approximately 42 % of drugs and drug candidates contain amine functional groups in their molecular structures [3]. For instance, amongst well established drugs containing amino groups: chlorpheniramine [3b,3c] is an antihistamine drug helping in releasing allergic ailments caused by cold, fever, itchy skin, insect bites whereas chlorpromazine is used to relieve nervousness, excitement, and even mental disorder. Several secondary amines *viz.* nortriptyline [3d], desipramine [3e], and amoxapine [3f], apart from besides tertiary amines amitriptyline, imipramine, lofepramine and clomipramine are used as an antidepressants drug [3 g]. Further reports demonstrate that substituted tryptamines and phenethylamines are key basic structures for a large variety of psychedelic drugs [3h]. Well known anesthetics such as morphine, codeine, and heroin contain tertiary amino groups. The US DEA has listed amphetamine, methamphetamine and methcathinone amines as controlled substances for psychostimulant [3i]. The chiral amines *viz.* ephedrine and phenylephrine are used to relieves congestion [3j]. Presumably, the amine moieties in the organic drugs helps in an active transportation of drug through the formation of organic ammonium cation.

Moreover, chirality has been playing an important role in the modern drug development because therapeutic activity of enantiomers differs severely in terms of toxicity and pharmacokinetics [4]. Recently, we have demonstrated on how chirality and redox potentials of enantiomers influences their anti-proliferative activity [5]. The chiral molecules present in the biological system (proteins) apparently recognise the enantiomers selectively and assist in the improved biological activity through ligand-protein bonding [5,6].

Moreover, Tumor Necrosis Factor Alpha (TNF-α) is a pleiotropic pro-

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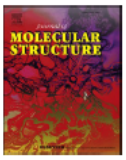
https://doi.org/10.1016/j.molstruc.2023.137165
Received 9 August 2023; Received in revised form 8 November 2023; Accepted 24 November 2023

Journal of Molecular Structure 1287 (2023) 135657

Contents lists available at ScienceDirect

Journal of Molecular Structure

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



Macrocyclic Ni^{II}-Xanthate [Ni$_2^{II}$-μ^2-bis-{($\kappa^2 S,S$-S$_2$COCH$_2$CH$_2$)$_2$N(Ts)}] Complex and a Cyclic Thiocarbonate Monomer: Synthesis, Crystallography, Photophysical, TD-DFT and Investigation of Thermochromism

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ARTICLE INFO

Keywords:
Organic/ inorganic macrocycles
XRD
Thermochromism
Electrochemical
TD-DFT

ABSTRACT

Potassium salt of N,N-Bis(2-dithiocarbonatoethyl)-4-methylbenzenesulfon amide (K$_2$xan) was synthesized and characterized prior to use in the progress of a 24-membered binuclear metallomacrocyclic compound [Ni$_2^{II}$-μ^2-bis-{($\kappa^2 S,S$-S$_2$COCH$_2$CH$_2$)$_2$N(Ts)}] (1) and a synthetically challenging 16-member organic functional macrocycle 6,14-ditosyl-1,3,9,11-tetraoxa-6,14-diaza-cyclohexadecane-2,10-dithione (2). Compounds have been characterized by using microanalysis, standard spectroscopic and crystallographic techniques. A plausible mechanism for the formation of compound 2 has been established based on experimental evidence. Compounds 1 and 2 fluoresces at 377 and 293 nm upon excitation at 314 and 232 nm, respectively. The single crystal X-ray diffraction (SCXRD) study revealed a distorted square planar coordination geometry around Ni^{II}-centre in 1 which is consistent in the solution of non-coordinating solvents such as CH$_2$Cl$_2$. In a coordinating solvent such as DMSO, however, charge transfer bands 421, 481 nm vanished and characteristic d-d transition band at 698 nm appeared which suggest a change in the coordination geometry around Ni^{II} centre from square planar (in CH$_2$Cl$_2$) to octahedral complex (in DMSO). This solvatochromic behaviour of Ni^{II}-xanthate complex 1 is supplemented by reversible thermochromic behaviour over a wide temperature *ca* 30–90°C. Notably, thermal degradation of Ni^{II}-xanthate complex 1 gave a stable residual mass that corresponds to NiS. The X-band EPR, UV–visible and TD-DFT studies and electrochemical investigations have been performed to rationalize the results and establish the structure-property correlation.

1. Introduction

The interest has been continued in the design and synthesis of diversified molecular structures with diverse sizes and shapes through self-assembly processes [1–5]. However, control over the arrangements of molecular fragments to obtain a discrete molecular structure has been stimulating to the synthetic chemists [6–7]. The metal-directed self-assembly process has emerged as one of the powerful methodology for the formation of multi-dimensional structural motifs that possess interesting physico-chemical properties [8–14].

In this connection, dithiocarbamates, with their ability to demonstrate a variable mode of binding and to stabilize the diverse oxidation states of various transition/ non-transition metal ions, have been efficiently utilized in the process leading to a wide variety of discrete molecular structures such as metallomacrocyclic [15–19], catenanes [20], cavitands [21], cryptands [22] and container molecules [23–24]. This signifies the extensive study of dithiocarbamates in metal directed self-assembly. However, isostructural xanthate ligands have scarcely been investigated. To date, literature evidences a single example of structurally characterized metallomacrocyclic complex based on xanthate ligand [25]. It underlines their synthetic challenge, despite the ready availability of xanthate ligands bearing functionalized backbone.

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https://doi.org/10.1016/j.molstruc.2023.135657
Received 22 February 2023; Received in revised form 22 April 2023; Accepted 24 April 2023

Inorganica Chimica Acta 543 (2022) 121139

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Research paper

New series of M^{II}-dithiocarbamate complexes ($M = Cu^{II}$, Ni^{II} and Zn^{II}) holding pendant *N,O*-Schiff base moieties: Synthesis, characterization, photophysical, crystallographic, anti-microbial and DFT study

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ARTICLE INFO

Keywords:
Dithiocarbamate
Transition metals
Spectroscopy
SCXRD
Antimicrobial
DFT

ABSTRACT

Multi-functional ligand precursors 2-[2-(1-piperazinyl)ethyliminomethyl] phenol (L^1), 1-[2-(1-piperazinyl)ethyliminomethyl]naphthlene-2-ol (L^2) and 6-methoxy-2-[2-(1-piperazinyl)ethyliminomethyl]phenol (L^3) were selected to derive a new series of binuclear and mononuclear M^{II}-dithiocarbamate complexes of the type [Cu{κ^2S,S-S_2C-piperazine-$C_2H_4N{=}C(H)(R)\}_2]_2$ (R = -Ph(OH) 1, -Naph(OH) 2, -Ph(OH)(OCH_3) 3 and [M{κ^2S,S-S_2C-piperazine-$C_2H_4N = C(H)(R)\}_2$] (R = -Ph(OH), M = Ni^{II} 4, Zn^{II} 5; R = -Naph(OH), M = Ni^{II} 6, Zn^{II} 7; R =- Ph(OH)(OCH_3), M = Ni^{II} 8, Zn^{II} 9). All the compounds have been characterized by microanalysis and standard spectroscopic methods such as ^1H and ^{13}C NMR, IR and UV–visible absorption spectroscopy. The molecular structures for L^1 and its Cu^{II}-/Ni^{II}-dithiocarbamate complexes 1 and 4 were elucidated by single crystal X-ray diffraction (SCXRD) and their crystal packing patterns were studied. Interestingly, molecules of L^1 forms 3D multiple open tubular supramolecular assembly by involving H bonding and other $NH\ldots O{=}C$, $CH_{benzene}\cdots O$ and $CH_{piperazine}\cdots O$ weak intermolecular forces. Notably, Zn^{II}-dithiocarabamate complexes give maximum emission in visible nm region (*ca* 444–489) upon excitation of ultraviolet radiation with concomitant Stock shift *ca* < 200 nm. Thermogravimetric study was performed on 1–9 to investigate their thermal stability and degradation patterns. All the compounds have been screened for their potential *in vitro* antimicrobial activity against by using *S. aureus, E. coli and C. albicans* by Broth dilution method. The density functional theory calculations have been carried out to reinforce the experimental outcomes.

1. Introduction

The interest in the chemistry utilizing dithiocarbamate ligands has been continued due to its involvement in formation of valuable synthetic products with transition metal ions present in different oxidation states [1]. Compounds derived from dithiocarbamates exhibit fascinating electrochemical, optical properties and various industrial applications such as lubricants, antioxidants, fungicides, accelerators for rubber vulcanization, and as photoluminescent materials [2]. Dithiocarbamate ligands have been widely exploited by several researchers in the supramolecular chemistry [3]. Many research groups [4,5] are extensively involved in searching dithiocarbamate complexes potential showing profound applications in the area of bio-medical sciences. The ability of dithiocarbamate ligands to stabilize both low- and high-valent metal ions is ascribed to the adoption of dithiocarbamate and thioureide tautomers. The localization of lone pair of electrons on sp^3 nitrogen atom with pyramidal arrangement of substituents makes dithiocarbamate as a soft donor ligand to bind with low-valent metal atoms while the delocalisation of lone pair of nitrogen over C—N—S atoms rehybridizes nitrogen to sp^2 nitrogen atom with planar arrangement of substituents makes thioureide as a hard donor ligand and able to bind with high-valent metal binding [4d].

Besides, the piperazine ring often appears to be a key component in biochemical development [6–8]. The effect of piperazine unit on the

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https://doi.org/10.1016/j.ica.2022.121139
Received 7 May 2022; Received in revised form 26 July 2022; Accepted 1 August 2022

❖ Papers presented in Conferences

1. **Presented Oral Presentation** in VIII All Gujarat Research Scholar's Meet at The Maharaja Sayajirao University of Baroda, Vadodara, **February 2023.**
2. **Participated** in National Seminar on Decadal Trends in Chemistry Research: The Perspective of Women Scientist (**W-CHEM-2020)** at The Maharaja Sayajirao University of Baroda, Vadodara, **March 2020.**
3. **Participated** in National Seminar on Advances in Chemistry of bioactive Molecules (ACBAM-2020) at The Maharaja Sayajirao University of Baroda, Vadodara, **January 2020.**
4. **Participated** in National workshop on Advanced Analytical Techniques for Elemental Analysis (AAT-2019) at The Maharaja Sayajirao University of Baroda, Vadodara, **December 2019.**
5. **Presented Poster Presentation** in International Conference on Advanced Functional Materials of Energy, Environment and Health Care (AFMEEHC) at University of Mysore, **March 2019.**
6. **Participated** in National Symposium on Advances in Chemical Research (ACR-2019) at The Maharaja Sayajirao University of Baroda, Vadodara, **February 2019.**
7. **Participated** in VII All Gujarat Research Scholars' Meet at The Maharaja Sayajirao University of Baroda, Vadodara, **February 2018.**
8. **Participated** in National Conference on Chirality (NCC-2017) at The Maharaja Sayajirao University of Baroda, Vadodara, **November 2017.**