



UNIVERSITI PUTRA MALAYSIA

**STRUCTURE ELUCIDATION AND BIOLOGICAL ACTIVITY OF
DITHIOCARBAZATE DERIVATIVES, THEIR
SCHIFF BASE LIGANDS AND METAL COMPLEXES**

KHOO TENG JIN

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**Structure Elucidation and Biological Activity of Dithiocarbazate Derivatives, Their
Schiff Base Ligands and Metal Complexes**

By

KHOO TENG JIN

**Thesis Submitted to the School of Graduate Studies,
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Dithiocarbazate Schiff base ligands and their complexes has been an active field of research concentrating on synthesis and characterization and their transition metal complexes. This work focuses on the synthesis and characterization of new dithiocarbazate ligands of *S*-3-picolyldithiocarbazate, *N*-Pyridin-3-ylmethylene-*N*-[5-(pyridine-3-ylmethylsulfanyl)-[1,3,4]thiadiazol-2-yl]-hydrazine, *S*-4-picolyldithiocarbazate and *N*'-Pyridin-4-ylmethylenehydrazinecarbodithioic acid pyridine-4-yl methylester. The Schiff bases were fully characterized using various physico-chemical and spectro-chemical analyses and its crystal structure elucidated. Work on these new Schiff base ligands has paved the way for further research into their complexes. A total of 56 complexes and 12 Schiff base ligands were synthesized each containing different functionalities which are, 4-aminoacetophenone, furyl and carboxyl and pyridine.



The synthesized and fully characterized Schiff bases and their complexes were then evaluated for their biological activities against antimicrobial and cytotoxicities studies. From the antimicrobial studies, Schiff bases have wider range of activity against the bacterial strains as compared to its complexes while complexes that comprises of d^{10} metals has the best potential as antimicrobial agent. In the evaluation of its cytotoxicities against selected cancer cell lines, copper(II), platinum(II) and palladium(II) metal complexes are strongly active with lowest CD_{50} values which are comparable to commercially available drugs. In conclusion, both the Schiff bases and their complexes can be further studied for its mechanism of action and has high potential to be developed into a much potent chemotherapeutic agents.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan Ijazah Doktor Falsafah

**ELUCIDASI STRUKTUR DAN AKTIVITI BIOLOGI LIGAN BASE SCHIFF
DAN LOGAM KOMPLEKS DERIVASI DITHIOCARBAZAT**

Oleh

KHOO TENG JIN

Oktober 2008

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Kajian terhadap dithiocarbazat base Schiff dan logam kompleks adalah bidang yang giat aktif dan tertumpu kepada sintesis dan penentuan struktur. Penyelidikan ini tertumpu kepada sintesis and penentuan struktur ligan dithiocarbazat yang baru yakni, *S*-3-picolildithiocarbazat, *N*-Pyridin-3-ylmethylene-*N*-[5-(pyridin-3-ylmethylsulfanyl)-[1,3,4]thiadiazol-2-yl]-hydrazin, *S*-4-picolildithiocarbazat dan *N*⁷-Pyridin-4-ylmethylenhydrazincarbodithioic acid pyridin-4-ylmethylester. Struktur base Schiff baru ini tentukan sepenuhnya menggunakan pelbagai teknik analisis kimia-fisikal dan spektrokimia. Penyelidikan ini telah berjaya membuka peluang kepada kajian yang lebih lanjut terhadap base Schiff dan logam kompleks baru ini. Sejumlah 56 kompleks dan 12 ligan base Schiff telah disintesis dimana ianya terdiri daripada pelbagai kumpulan berfungsi iaitu, 4-aminasetophinon, furil, carboxil dan piridin.

Ligan base Schiff dan kompleks logam yang telah ditentukan sepenuhnya telah dikaji untuk aktiviti biologinya terhadap antimikrob dan sitotoksik. Keputusan antimikrob



menunjukkan base Schiff mempunyai aktiviti yang lebih meluas terhadap jenis bakteria berbanding kompleks logamnya tetapi kompleks logam yang terdiri daripada logam transisi d^{10} lebih berpotensi sebagai agen antimikrob. Dalam kajian sitotoksik terhadap sel kanser yang dipilih, kompleks-kompleks logam yang terdiri dari kuprum(II), platinum(II) dan palladium(II) didapati amat active dengan nilai CD_{50} yang amat rendah dan boleh dibandingkan dengan nilai ubat antikanser komersial. Dengan ini, boleh disimpulkan bahawa ligan base Schiff dan logam kompleksnya boleh dilanjutkan kajian untuk menentukan mekanisma tindakan dan kedua-duanya mempunyai potensi yang tinggi untuk dibangunkan sebagai ajen kemoterapi.



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This work would not have any significant if not for the support and love from my parents, sisters and my wife. Thank you all for allowing me to come this far. This work is dedicated to you all.



For my grandparents, parents, sisters, wife and supervisors

Possibly, just possibly,

this is the chemistry of love



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1. INTRODUCTION

Schiff bases are a diverse class of ligands containing O, N as well as S as their main donor atoms for chelation [1]. With this simple property, they have opened a wide and active field of studies in inorganic chemistry. This field of research continues to prosper because of continuous discovery of applications in a wide variety of fields specifically pharmaceuticals, agricultural chemicals and electronics. A more defined scope of research concentrates on synthesis and characterization of complexes containing nitrogen-sulfur donor ligands with transition metals and their properties. In many cases, there are significant differences in bioactivity after complexation.

Schiff bases of dithiocarbazate acid derivatives are one of these types of ligands. The structure is shown in Figure 1.1 where R = methyl, benzyl or pyridine.

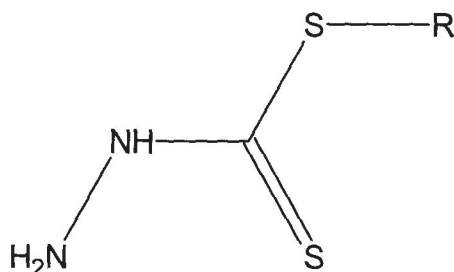


Figure 1.1: Dithiocarbazate acid derivatives

In the solid state, dithiocarbazates were found to exist only as *cis-trans* and *trans-cis* isomers [2, 3] although theoretically they can evolve as four different types of isomers as shown in Figure 1.2. Conformation is assigned with respect to the N-C and C-S bond.

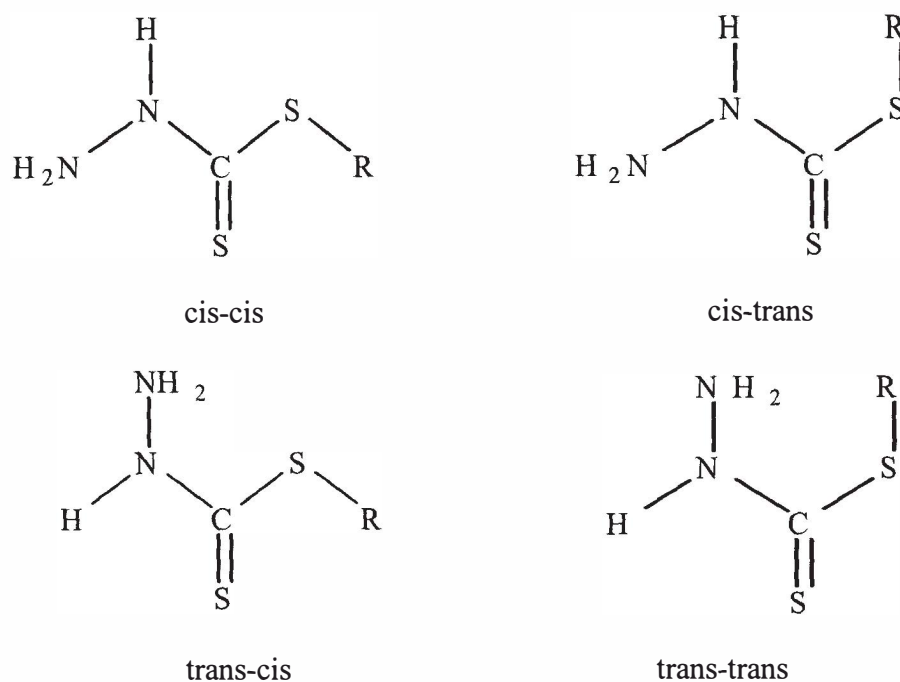


Figure 1.2: Possible isomers of dithiocarbazates

The types of isomers isolated are expected to be determined by the method of preparation and temperature of recrystallization. The *cis-trans* isomer was formed by recrystallization from benzene/chloroform solvent at room temperature while *trans-cis* was formed by recrystallization from methanol-water solvent in the ratio of 1:3 at -20°C . Using S-methyldithiocarbazate as an example, X-ray diffraction studies found the *cis-trans* conformers crystallize as a monoclinic, the space group $C 2/c$ with $Z' = 8$. The basic units of these structures are centrosymmetric dimers formed by $\text{NH}\cdots\text{N}$ hydrogen bonds. The component monomers are in the *cis-trans* conformation, where the group $-\text{NH}-\text{NH}_2$ bends toward C-S and the SMe towards the opposite side. In a second conformer (*trans-cis*) of S-methyldithiocarbazate, the crystal has been obtained by crystallisation at low temperature and is triclinic with $Z' = 2$. The structure comprises centrosymmetric dimers linked by $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds, in contrast to the *cis-trans*

conformer where N-H·····N bonds are present. The vibrational spectra of both conformers differ markedly, but the change of conformation does not significantly alter the bond distances and angles of either structure. In solution, dithiocarbazate derivatives undergo thione-thiol tautomerism depending on the pH of the solution (Figure 1.3), while in the solid state, only the thione tautomer exists.

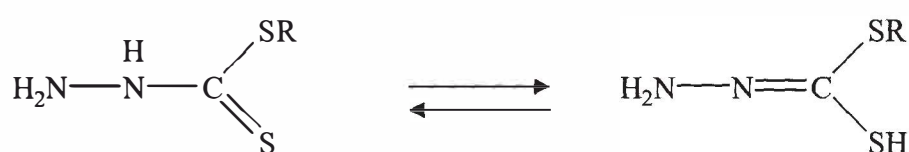


Figure 1.3: thione-thiol tautomerism

Dithiocarbazate derivatives have four donor atoms which are available to chelate with metal ions. Only two may ligate at a given time. Therefore, there are two possible complexation modes which are sulfur and β -nitrogen (NS) modes or both sulfur atoms (SS) mode (Figure 1.4). However, there are no examples of complexes of Schiff bases derived from *S*-alkyl ester of dithiocarbazic acid in which both sulfur atoms are coordinated to a metal ion.

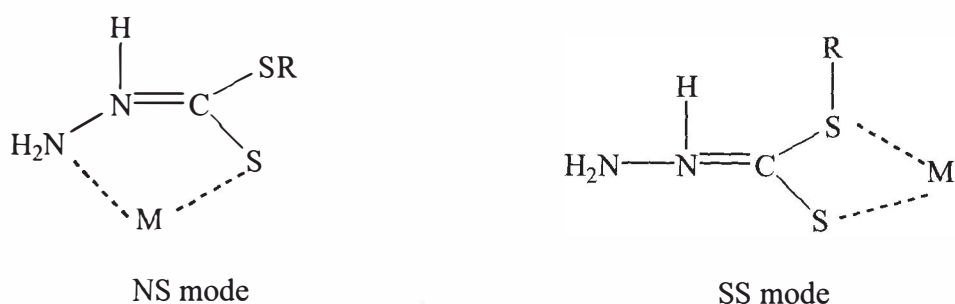


Figure 1.4: Complexation modes of dithiocarbazate derivatives

A wide series of compounds with interesting chemical properties can be derived by substituting the –R group using R-halides while larger Schiff base molecules can be derived by using varieties of organic aldehydes or ketones in the condensation reaction. Interesting properties and geometries can be modified by chelating to different transition metals. These fascinating properties of the ligands forming different geometries, crystal morphologies and biological properties even though their molecular structures differ only slightly gave us the motivation for further research.

This thesis will discuss the synthesis of new ligand types containing 2-, 3- and 4- isomers of picoline substituted for –R, Schiff bases derived from these compounds through condensation reaction with different carbonyl compounds and complexation of the derivatives with transition metals Ni(II), Cu(II), Zn(II), Cd(II), Pd(II) and Pt(II). This will be followed by discussion of the characterization of the compounds and structure elucidation using various physico-chemical and spectroscopic techniques and the Single Crystal X-ray Diffraction (SXRD) methods when suitable single-crystals could be isolated. The thermal and electrochemical behaviors in solid and solution are also explored as well as their biological properties (qualitatively and quantitatively). Selected functional groups containing aminoacetophenone, fural, carbonyl, pyrrole and pyridine were introduced into the Schiff bases to study the effect of the presence of different functional groups in relation to biological activity.

It is hoped that this project will give a new dimension to this field of research and complement work done previously by our group and by other groups in addition to opening up new avenue for research in this area.



In more specific the objectives of this research are:

- (a) To synthesize new ligands derived from dithiocarbazate containing isomers of pyridine.
- (b) To synthesize new series of Schiff bases containing aminoacetophenone, fural, carbonyl, pyrrole and pyridine.
- (c) To synthesize complexes with transition metals of Ni(II), Cu(II), Zn(II) Cd(II), Pd(II) and Pt(II).
- (d) To characterize and elucidate the structure of the synthesized compound using various physico-chemical, spectroscopic and Single Crystal X-ray Crystallographic (SXRD) method.
- (e) To evaluate the qualitative and quantitative antimicrobial activities of the Schiff bases and their complexes.
- (f) To evaluate the cytotoxicity of the synthesized compound against cancer cell lines and
- (g) To correlate the biological activity with the structure of the synthesized compound.



2. LITERATURE REVIEW

2.1 Multidentate Nitrogen-Sulfur Donor Ligands their Metal Complexes and Crystal Structures

One of the least understood properties of this type of ligand is their chelating property which ranges from bidentate to multidentate. Although other physico-chemical methods are helpful in determining multidentate chelating capabilities, the best way to understand its chelating properties is by Single Crystal X-ray Diffraction (SXRD). The number of donor atoms in the Schiff base depends on the type of aldehyde or ketone condensed with the dithiocarbazic acid. A good representative of this type of ligation is in the bis{*S*-methyl- β -*N*-(6-methylpyrid-2-yl)-methylenedithiocarbazato}nickel(II) complex [4]. The uninegatively charged tridentate ligand formed by the condensation reaction between 6-methyl-2-formylpyridine with *S*-methyl and *S*-benzylthiocarbazates has the structure shown in Figure 1.5 [4].

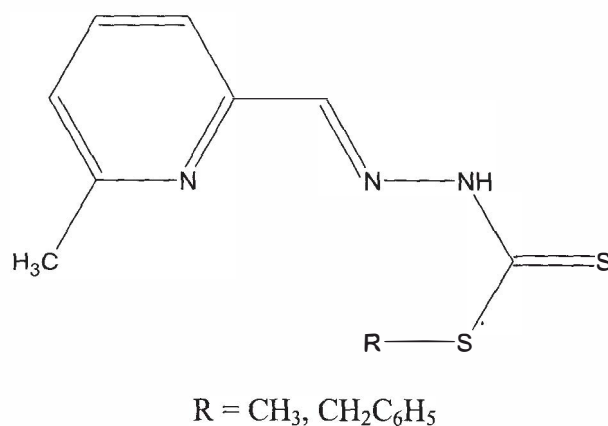


Figure 1.5: The structure of *S*-alkyl- β -*N*-(6-methylpyrid-2-yl)-methylenedithiocarbazate

In the above case, the presence of 6-methylpyridine gives the ligand tridentate character through ligation of the mercaptide sulfur, azomethine nitrogen and the nitrogen

of the pyridine (NNS⁻) upon coordination with Ni(II) metal. The free Schiff bases does not display the $\nu(\text{SH})$ band at $\sim 2700 \text{ cm}^{-1}$ but exhibits $\nu(\text{NH})$ bands in the range $3100\text{-}3150 \text{ cm}^{-1}$ indicating that in the solid state it exists as a thioketo tautomer. Attempts by the author and his group to yield a mono-ligated Ni(II) complex with Cl⁻, Br⁻ or NCS⁻ as counter ion using large excess of Ni(II) salt always yielded the bis-ligated complex. This is in contrast to behavior seen for other related tridentate Schiff bases derived from 2-formylpyridine and S-methyl or S-benzyl-dithiocarbamate [5] which readily yielded the mono-ligated Ni(II) complex with a formula [Ni(NNS)X] where X = Cl, Br, NCS and I. The coordination modes of both complexes are determined by means of infrared spectra. Both types of complexes shows a shift in azomethine $\nu(\text{C}=\text{N})$ bands of the ligands to lower frequency and the increase in frequency of the hydrazinic N-N bond as a consequence of reduction between lone pairs of electrons on the hydrazine nitrogen atoms, supporting coordination *via* azomethine nitrogen atom. Coordination modes are further explained by means of structure elucidation using SXRD. The crystal structure of bis{S-methyl- β -N-(6-methylpyrid-2-yl)-methylenedithiocarbazato}nickel(II) is a six-coordinate environment with two Schiff base ligands coordinated to the nickel(II) ion as tridentate NNS chelating agents as shown in Figure 1.6. While the Schiff base coordinates in the iminothiolate form, a negative charge generated upon deprotonation is delocalized over the C-N-N-C bonds as indicated by intermediate bond distances of N-N = 1.389(9) Å, C-N = 1.26(1) Å and N-C = 1.31(1) Å, with the primary effect on the C-N bonds. By using SXRD, we are given the privilege to study the geometry of complexes, as in this case, the ligands are coordinated in the meridional configurations (with two azomethine nitrogen atoms *trans* to each other and the pyridine and sulfur atoms *cis*). This *mer* configuration has also been observed in nickel(II) complexes of

