



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS, CHARACTERISATION AND BIOLOGICAL ACTIVITIES OF
NITROGEN-SULPHUR LIGANDS AND THEIR TRANSITION METAL
COMPLEXES**

THAHIRA BEGUM

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COMPLEXES**

By

THAHIRA BEGUM

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

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THAHIRA BEGUM

September 2008

Chairman: Prof. Dr. Karen A.Crouse., Ph.D.

Faculty: Science

Synthetic compounds, especially those containing heterocyclic ring systems composed of nitrogen and sulphur have been of great interest due to their versatility as medicinal drugs. In view of this, three new isomeric dithiocarbazate ligands, S-2-methylbenzylthiocarbazate, S-3-methylbenzylthio- carbazate and S-4-methylbenzylthiocarbazate, twenty-one Schiff bases derived from the isomeric dithiocarbazates with pyridine-2-aldehyde, 6-methylpyridine-2-aldehyde, 2-benzoylpyridine, di-2-pyridylketone, 2-acetylpyridine, 3-acetylpyridine and 4-acetylpyridine, and their Cu(II), Ni(II), Zn(II) and Cd(II) complexes have been successfully synthesized in a 1:1 mol ratio in an ethanol/acetonitrile mixture and characterized *via* various physico-chemical and spectroscopic techniques. The NMR and mass spectral analysis of the isomeric dithiocarbazates and their Schiff bases indicated the presence of a cyclised compound which was then identified as 2,5-bis(n-methylbenzylthio)-1,3,4-thiadiazole (n= 2,3 or 4). Elemental analyses, magnetic and spectral data indicate an octahedral geometry for all the metal



complexes, except those derived from 3-acetylpyridine and 4-acetylpyridine which were expected to possess a distorted square-planar geometry. The structures of five Schiff bases, ten transition metal complexes and two thiadiazoles, namely 2,5-bis(2-methylbenzylthio)-1,3,4-thiadiazole and 2,5-bis(4-methylbenzylthio)-1,3,4-thiadiazole were successfully elucidated via X-ray crystallographic analysis. The transition metal complexes had distorted octahedral geometries, coordinating *via* the pyridyl nitrogen, azomethine nitrogen and thiolate sulphur atoms of the Schiff bases in a *mer* configuration. The complexes have been evaluated for their biological activities against seven pathogenic microbials and two breast cancer cell lines, MCF-7 (Human breast carcinoma cells with positive estrogen receptor) and MDA-MB-231 (Human breast carcinoma cells with negative estrogen receptor). The complexes were mostly antibacterial, but were inactive against the fungal strains tested. The Schiff bases in this study were also completely inactive against the microbial strains but complexation with the transition metal ions had significantly increased the activity. The complexes were generally more active against the MCF-7 cell line as compared to the MDA-MB-231 cell line. Several correlations based on the structure-bioactivity relationship of the complexes have been made.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Falsafah Kedoktoran.

SINTESIS, PENCIRIAN DAN AKTIVITI BIOLOGI LIGAN NITROGEN-SULFUR DAN KOMPLEKS LOGAM PERALIHAN MASING-MASING

Oleh

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Bahan sintetik yang mengandungi nitrogen dan sulfur di dalam sistem gelang heterosikliknya telah menarik minat ramai penyelidik kerana kepelbagaian fungsinya sebagai ubat rawatan. Tiga isomer ligan ditiokarbamat baru, *S*-2-metilbenzilditiokarbamat, *S*-3-metilbenzilditiokarbamat dan *S*-4-metilbenzilditiokarbamat, dua puluh satu bes Schiff disediakan daripada isomer ditiokarbamat dengan piridina-2-aldehid, 6-metilpiridina-2-aldehid, 2-benzoilpiridina, di-2piridilketon, 2-asetilpiridina, 3-asetilpiridina dan 4-asetilpiridina dan kompleks logam Cu(II), Ni(II), Zn(II) dan Cd(II) masing-masing telah berjaya disintesis dengan nisbah 1:1 mol di dalam campuran pelarut etanol/asetonitril dan dicirikan menggunakan pelbagai teknik kimia-fizik dan spektroskopi. Analisis resonan kemagnetan nuklear dan spektra jisim terhadap isomer ditiokarbamat dan bes Schiff menunjukkan kehadiran sebatian siklik dikenali sebagai 2,5-bis(*n*-metilbenziltio)-1,3,4-tiadiazol (*n*=2,3 atau 4). Analisis unsur C,H,N,S dan peratus logam, kerentanan magnet dan data spektral menunjukkan semua kompleks mempunyai geometri oktahedral kecuali kompleks logam daripada terbitan 3-asetilpiridina dan 4-asetilpiridina dan dicadangkan



mempunyai geometri segi empat satah terherot. Lima struktur bes Schiff, sepuluh kompleks logam dan dua tiadiazol iaitu 2,5-bis(2-metilbenziltio)-1,3,4-tiadiazol dan 2,5-bis(4-metilbenziltio)-1,3,4-tiadiazol telah berjaya ditentukan dengan menggunakan teknik kristalografi sinar-X. Kompleks logam peralihan mempunyai geometri oktahedral terherot, mengkoordinat kepada bes Schiff melalui nitrogen piridil, nitrogen azometin dan atom tiolat sulfur dalam konfigurasi *mer*. Semua kompleks logam telah disaring untuk aktiviti biologi terhadap tujuh mikroba dan dua sel barah payudara, MCF-7 (sel barah manusia dengan penerima estrogen positif) dan MDA-MB-231 (sel barah manusia dengan penerima estrogen negatif). Didapati bahawa kebanyakan kompleks logam adalah aktif terhadap bakteria tetapi tidak aktif terhadap semua kulat yang disaring. Bes Schiff dalam kajian ini juga didapati tidak aktif terhadap mikroba tetapi setelah membentuk kompleks dengan ion logam peralihan, kompleks logam ini telah menunjukkan pertambahan aktiviti yang signifikan. Secara umumnya, kompleks logam adalah lebih aktif terhadap sel MCF-7 dibandingkan dengan sel MDA-MB-231. Beberapa perkaitan berdasarkan kepada hubungan aktiviti bio-struktur kompleks logam telah dibincangkan.



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DECLARATION

I declare that the thesis is my original work except for the quotations and citations, which have been duly acknowledged. I also declare that this it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institutions.

THAHIRA BEGUM

Date:

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C8	UV/Visible Spectrum of py2alS3M(10^{-4} M)	254
C9	UV/Visible Spectrum of Cu(py2alS3M)(10^{-3} M)	254
C10	UV/Visible Spectrum of Ni(py2alS3M)(10^{-3} M)	254
C11	UV/Visible Spectrum of Ni(py2alS3M)(10^{-4} M)	254
C12	UV/Visible Spectrum of Zn(py2alS3M)(10^{-4} M)	254
C13	UV/Visible Spectrum of Cd(py2alS3M)(10^{-4} M)	255
C14	UV/Visible Spectrum of py2alS4M(10^{-4} M)	255
C15	UV/Visible Spectrum of Cu(py2alS4M)(10^{-3} M)	255
C16	UV/Visible Spectrum of Cu(py2alS4M)(10^{-4} M)	255
C17	UV/Visible Spectrum of Ni(py2alS4M)(10^{-3} M)	255
C18	UV/Visible Spectrum of Ni(py2alS4M)(10^{-4} M)	255
C19	UV/Visible Spectrum of Zn(py2alS4M)(10^{-4} M)	256
C20	UV/Visible Spectrum of Cd(py2alS4M)(10^{-4} M)	256
C21	UV/Visible Spectrum of 6mpyS2M(10^{-3} M)	256
C22	UV/Visible Spectrum of Cu(6mpyS2M)(10^{-4} M)	256



C23	UV/Visible Spectrum of Ni(6mpyS2M)(10 ⁻³ M)	256
C24	UV/Visible Spectrum of Ni(6mpyS2M)(10 ⁻⁴ M)	256
C25	UV/Visible Spectrum of Zn(6mpyS2M)(10 ⁻⁴ M)	257
C26	UV/Visible Spectrum of Cd(6mpyS2M)(10 ⁻⁴ M)	257
C27	UV/Visible Spectrum of 6mpyS3M(10 ⁻⁴ M)	257
C28	UV/Visible Spectrum of Cu(6mpyS3M)(10 ⁻³ M)	257
C29	UV/Visible Spectrum of Ni(6mpyS3M)(10 ⁻³ M)	257
C30	UV/Visible Spectrum of Ni(6mpyS3M)(10 ⁻⁴ M)	257
C31	UV/Visible Spectrum of Zn(6mpyS3M)(10 ⁻⁴ M)	258
C32	UV/Visible Spectrum of Cd(6mpyS3M)(10 ⁻⁴ M)	258
C33	UV/Visible Spectrum of 6mpyS4M(10 ⁻⁴ M)	258
C34	UV/Visible Spectrum of Cu(6mpyS4M)(10 ⁻³ M)	258
C35	UV/Visible Spectrum of Cu(6mpyS4M)(10 ⁻⁴ M)	258
C36	UV/Visible Spectrum of Ni(6mpyS4M)(10 ⁻³ M)	258
C37	UV/Visible Spectrum of Ni(6mpyS4M)(10 ⁻⁴ M)	259
C38	UV/Visible Spectrum of Zn(6mpyS4M)(10 ⁻⁴ M)	259
C39	UV/Visible Spectrum of Cd(6mpyS4M)(10 ⁻⁴ M)	259
C40	UV/Visible Spectrum of 2bzpS2M(10 ⁻⁴ M)	259
C41	UV/Visible Spectrum of Cu(2bzpS2M)(10 ⁻³ M)	259
C42	UV/Visible Spectrum of Cu(2bzpS2M)(10 ⁻⁴ M)	259
C43	UV/Visible Spectrum of Ni(2bzpS2M)(10 ⁻³ M)	260
C44	UV/Visible Spectrum of Ni(2bzpS2M)(10 ⁻⁴ M)	260
C45	UV/Visible Spectrum of Zn(2bzpS2M)(10 ⁻⁴ M)	260
C46	UV/Visible Spectrum of Cd(2bzpS2M)(10 ⁻⁴ M)	260

