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**FUNCTIONALIZED INDOLES: HETERO- AND MACROCYCLIZATION,  
COORDINATION CHEMISTRY, AND BIOLOGICAL PROPERTIES**

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## ABSTRACT

Three indolyl-imine ligands have been synthesized through the condensation of S-benzylthiocarbamate with indole-2-carbaldehyde, indole-3-carbaldehyde and indole-7-carbaldehyde. Treatment of these Schiff bases with acetate salts of Ni(II), Zn(II) and Cd(II) in ethanol yielded a series of complexes of 2:1 type (ligand/metal ratio) in which the ligands coordinated to the metal ions as monoanionic *N,S*-bidentate chelates. While the 2-imineindole and 3-imineindole formed the expected five-membered chelate rings, the X-ray crystal structure of  $[\text{Cd}(\text{HL}^3)(\text{py})_2]$ , ( $\text{HL}^3$  = the mono-deprotonated 7-imineindole), revealed an unusual mode of coordination, namely formation of four-membered rings with the metal atom. Reaction of the 7-imineindole with the metal ions in the presence of potassium hydroxide produced complexes of the type  $[\text{M}(\text{L}^3)(\text{H}_2\text{O})]$  in which the Schiff base acts as a dianionic *N,N,S*-tridentate ligand.

A new series of gallic hydrazones containing an indole moiety was synthesized through the reaction of gallic hydrazide and different indole carboxaldehydes. Their antioxidant activities were determined on DPPH radical scavenging and inhibition of lipid peroxidation. The *in-vitro* cytotoxic activities of the compounds were evaluated against HCT-116 (human colon cancer cell line) and MCF-7 (estrogen-dependent human breast cancer cell line) by the MTT method. An attempt was made to correlate the biological results with their structural characteristics. A limited positive structure activity relationship was found between cytotoxic and antioxidant activities.

The reaction of the potential multidentate ligand, 2-(diformylmethylene)-3,3-dimethylindole (diformyl) with  $M(\text{OAc})_2$  ( $M = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}},$  and  $\text{Pd}^{\text{II}}$ ) afforded a series of metal complexes with different nuclearity in which the mono-deprotonated diformyl behaves as an *N,O*-bidentate chelate or *N,O,O*-tridentate chelating-bridging agent. The bonding modes of the ligand and thus the structures could be modified to some extent by further treatment of the complexes with an ancillary ligand (methanol, pyridine, or 4,4-bipyridine). In the case of the palladium(II) complex, the pyridine and 4,4-bipyridine adducts yielded *C,N*-chelation of the metal ion through the aldehyde carbon and indolic nitrogen of the doubly deprotonated diformyl. The resulting acyl-palladium complexes were further bridged into polymeric structures when the dianionic diformyl behaved as a *C,N,O*-chelating-bridging ligand.

A series of new pyrazolyndolenine derivatives has been synthesized through the reaction of 2-(diformylmethylidene)-3,3-dimethylindole (diformyl) with six different hydrazides. Whereas the reaction of *p*-toluenesulfonylhydrazide and *S*-benzylthiocarbazide with diformyl yielded the expected pyrazolyndolenines as the sole products, the initial products of the reactions of diformyl with semicarbazide, thiosemicarbazide, and carbohydrazide underwent cleavage. The reaction of diformyl with thiocarbohydrazide resulted in a unique one-pot formation of pyrazole and thiadiazole rings, conjugated with the indolenine component. The solid state structures of these heterocycles were established by X-ray crystallographic analysis.

Starting from 2-(diformylmethylidene)-3,3-dimethylindole, a new dibenzotetraaza[14]annulene having indolenine moieties has been synthesized. The ligand

provided two different coordination sites thus, depending on the entity of the metal ions different bonding modes occurred resulting in variety architectures. The molecular structures of the compounds have been determined by X-ray crystallographic analysis.

## ABSTRAK

Tiga ligan indolil-imin telah disintesis melalui kondensasi S-benzilditiokarbamat dengan indol-2-karbaldhid, indol-3-karbaldhid dan indol-7-karbaldhid. Tindak balas bes Schiff ini dengan garam asetat Ni(II), Zn(II) and Cd(II) dalam etanol menghasil siri kompleks (dimana nisbah ligan/logam 2:1) dimana ligannnya berkoordinat kepada logam sebagai monoanionik kelat *N,S*-bidentat. Ligan 2-iminindol dan 3-iminindol pula membentuk gelang kelat lima-ahli yang dijangkakan, struktur X-sinaran  $[Cd(HL^3)(py)_2]$ , ( $HL^3$  = mono-terdiprotonat 7-iminindol), mempamerkan mod koordinatan yang luar biasa, iaitu pembentukan gelang empat-ahli dengan atom logam. Tindak balas 7-iminindol dengan ion logam dengan kehadiran kalium hidroksida menghasil kompleks  $[M(L^3)(H_2O)]$  dimana bes Schiff bertindak sebagai ligan dwianionik *N,N,S*-tridentat.

Satu siri baru gallik hydrazon yang mengandungi moiety indole telah disediakan melalui tindak balas gallik hydrazid dengan indol karboksaldhid yang berlainan. Aktiviti antipengoksidaannya telah ditentukan melalui pengaut radikal DPPH dan perencatan lipid peroksidaan. Aktiviti sitotoksik *in-vitro* sebatian ini dinilai melalui HCT-116 (sel cancer usus besar manusia) dan MCF-7 (sel cancer payudara manusia yang bergantung kepada estrogen) dengan kaedah MTT. Satu percubaan untuk mengaitkan aktiviti biologi dengan ciri struktur telah dilakukan. Hubung kait aktiviti dengan struktur yang positif lagi terhad ditemui di antara sitotoksik dengan aktiviti antipengoksidaannya.

Tindak balas ligan multidentat berpotensi, 2-(diformilmetilen)-3,3-dimetilindol (diformil) dengan  $M(OAc)_2$  ( $M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II},$  and  $Pd^{II}$ ) menghasil satu siri

kompleks logam dengan nukleariti yang berlainan dimana diformil mono-deprotonat bertindak sebagai *N,O*-kelat bidentat atau agen kelat-titian *N,O,O*-tridentat. Mod ikatan ligan dan strukturnya boleh diubah suai melalui tindak balas kompleks ini seterusnya dengan ligan ansillari (metanol, piridina, atau 4,4-bipiridina). Bagi kes kompleks palladium(II), aduk piridina dan 4,4-bipiridina menghasilkan *C,N*-kelatan dengan ion logam melalui karbon aldehyd dan nitrogen indolik diformil dubel deprotonat. Kompleks asil-palladium yang terhasil, seterusnya membentuk titian kompleks berstruktur polimer apabila dianionik diformil bertindak sebagai ligan *C,N,O*-kelatan-titian.

Satu siri terbitan pirazolilindolenin yang baru telah disintesis melalui tindak balas 2-(diformilmetiliden)-3,3-dimetilindol (diformil) dengan enam hidrazid yang berlainan. Tindak balas *p*-toluensulfonilhidrazid dan *S*-benzilditiokarbazid dengan diformil menghasilkan pirazolilindolenin yang dijangkakan sebagai hasil utama, hasil permulaan tindak balas diformil dengan semikarbazid, tiosemikarbazid dan karbohidrazid melalui tindak balas belahan. Tindak balas diformil dengan tiokarbhidrazid membentuk satu-pot gelang pirazol dan tiadiazol, berkonjugat dengan komponen indolenin. Struktur pepejal heterosikel ditentukan dengan analisis X-sinaran kristallografi.

Bermula daripada 2-(diformilmetiliden)-3,3-dimetilindol, dibenzotetraaza[14]annulen yang terbaru serta mempunyai moiety indolenin telah disintesis. Ligan ini menyediakan dua tapak koordinatan, bergantung kepada entity ion logam membentuk mod koordinatan yang menghasilkan pelbagai arkitektur. Struktur molekul sebatian ini ditentukan dengan analisis X-sinaran kristallografi.

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