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THIAZOLE METAL COMPLEXES AND THEIR BIOLOGICAL APPLICATIONS

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Abstract:
The most imperative outcomes of extensive sturdies' (synthesis, spectral, structural characterization and biological applications) of metal complexes with thiazole derived ligands are reviewed. A large number of coordination compounds are known but still there is a need of new compounds to develop various efforts in different fields for biomedical applications. Schiff bases are generally bi-or tri- dentate ligands capable of forming very stable complexes with transition metals. Some are used as liquid crystals. In organic synthesis, Schiff base reactions are useful in making carbon-nitrogen bond.
Keywords: *thiazole, coordination, Schiff bases, organic synthesis*

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INTRODUCTION:

Thiazoles (–N=C–S) containing moiety has been employed as antipsychotic and antibacterial. Thiazole derivatives, particularly amino thiazoles, play vital role in pharmaceutical practice owing to their wide biological activities [1–4] like fungicidal, antimicrobial, antituber culosis, anticancer and antiinflammatory [5, 6]. For example, ritonavir an antiHIV drug contains a 5substi tuted oxymethylthiazole moiety, and an isostere of the important insecticide, imidacloprid has 2chloro5substituted methylthiazole as part of the molecule. Structure of some cited drug molecules are illustrated below: S N N H The substituted thiazoles compounds have a number of characteristic pharmacological features, such as relative stability and ease of starting materials, built in biocidal unit, enhanced lipid solubility with hydrophilicity, easy metabolism of compounds. The first syn theses of the thiazolic ring were made at the end of the nineteenth century when the initial research was car ried out by scientists, such as Hantzsch, Hubacher, Traumann, Miolatti, Tcherniac, and Gabriel. The derivatives of pyridine and thiazoles soon constituted an important part of heterocyclic chemistry, as much from the point of view of the initial research as from the practical aspect. Their biological and pharmaceutical interest is in fact important as they appear in the composition of certain vitamins, such as vitamin B1 (thiamine) and in the penicillin's. Reduced thiazoles serve in the study of polypeptides and proteins and oc cur as structural units in compounds of biological significance, for example, firefly luciferins and in antibiot ics bacitracin A and thiostrepton. Equally, some derivatives of the 2aminothiazoles are used as fungicides, pesticides, and bacteriocides, and others possess mi to depressive and mitostatic properties, and a large range of 2amino (and hydrazino) nitrothiazoles (nitridazole) are devoid of schistosomicidal activity. Certain Schiff bases derived from 2amino5phe nylthiazole and their reduction products show diuretic properties [7-12]. Others such as rhodanines are used as in termediates in the synthesis of amino acids, peptides, and purines. In industry, several mercaptothiazole de rivatives serve to accelerate the vulcanization of rub ber, and alkyl and acylthiazoles are known to be inter esting flavoring agents. Finally, derivatives of thiazole are also to be found in certain natural products: a new amino acid incorporating the thiazole ring has been recently isolated from the fungus Xerocomus subto mentosus. Syntheses of thiazoles have been carefully reviewed by Wiley et al., and in 1957 the subject was dealt with in an excellent survey by Sprague and Land. This list was usefully supplemented in 1970, 1973, and 1975 by the publications of Kurzer, and a number of books on penicillin contain much information on the reduced thiazole system. Asinger and Offermanns have reviewed the chemistry of d3 thiazolines, and Ohta and Kato's comprehensive survey on sydnones includes a section of mesoionic thiazoles[13-17].

Coordination behavior of thiazole

Thiazole, C3H3NS, first described by Hantzsch and Weber in 1887 (Arthur Rudolf Hantzsch (1857–1935) is among the lengthy list of important late 19th and early 20th century German chemists. Besides his synthesis of thiazole, his name has been attached to a pyridine synthesis, and to a pyrrole synthesis [18-20]. The Hantzsch thiazole synthesis is still important, today is a five membered aromatic heterocyclic (contains noncarbon atoms in the ring) organic compound that is useful in the manufacture of pesticides, drugs, dyes and other compounds. Some of them exhibit antitu mor and antiviral properties. Two modes of coordination must be considered for the system, bonding through nitrogen and sulphur donors. The majority of Schiff bases of 2aminothiazole derivatives are obtained in good yield by condensation of aqueous and alcoholic solution. Since 2aminothiazole has an additional potential coordination site in the amino nitro gen, it was considered worthwhile to study the complexes of this ligand.

Scope of Thiazole derived ligands

Parkinson's disease (PD) is the most common neurodegenerative movement disorder, characterized by a specific loss of dopaminergic neurons in the substantianigra pars compacta and affecting the population above the age of 60 years [21]. The major clinical symptoms of PD include bradykinesia, postural instability, rigidity and tremor. Furthermore, a number of patients also suffer from anxiety, depression, autonomic disturbances, and dementia. The underlying cause of this selective cell death is not understood pharmacological therapy of PD is presently aimed at symptomatic control because clinically effective neuro protectants capable of slowing the progression of ni gral dopaminergic neuron degeneration are yet to be identified. An alternative approach to the treatment of this disorder would be the use of neuroprotective or antioxidant therapy to prevent or slow down the de generation of these neurons. For many years, thiazole derivatives have been the subject of most structural and medicinal studies because of their biological potential. They are of interest as potential neuroprotective agents [22] as well as the possible core skeletons of ad enosine receptor antagonists with moderate affinity and selectivity at the A2A receptor

site [74]. Benzothi azoles are highly interesting molecules for drug development, because they are known to be useful for treat ing neurodegenerative disorders [75]. Among the most efficient compounds, lubeluzole has been shown exper imentally to preserve neurological function and reduce infarct volume in animal models of focal brain ischemia [76], while other derivatives, such as KHG21834 were capable of protecting PC12 cells and cortical and mes encephalic neurons from amyloid binduced degeneration [23].

Spectral Characteristics

Magnetic moment and electronic spectra. When the crystal structure is formed, magnetic moment of a giv en ion participating in this structure depends on oxidation state, the symmetry and the strength of the crystal field and the nature of the chemical bond. The nature of ligand field around the metal ion and geometry of metal complexes have been deduced from the electronic spectra [24] and magnetic moment data of the complexes. Electronic spectral data of the thiazole derived ligands and their metal complexes which con tained absorption reasons, band assignments and proposed geometry of the complexes. Ligands show strong peaks at 448, 380, and 259 nm. The two strong bands are attributed to the benzene π–π* and imino π–π* transitions. These bands are not significantly af fected by the chelation and also know intraligand charge transfer (ILCT), the third band in the spectra of the ligand is assigned to the n–π* transition. In the metal complexes this band shifted to a longer wave length with increasing intensity. This shift may be at tributed to the donation of lone pairs of electron of ni trogen atoms of the ligands to the metal ions.

IR Spectroscopy.

Practically all the ligands and metal complexes have been characterized in detail by recording their IR spectra. The infrared spectra of ligands show a band around 3450–3250 cm–1 due to hydrogen bonding. The ligands show bands in the regions 3250–3050 cm–1 assigned to the ν(N–H) of hy drazine or ν(N–H) imidazole moiety. The free ligands shows absorption bands in the range ~1650 cm–1 characteristics of azomethine (C=N) group. The band due to the thiazole ring (C=N) was absorbed in the range 1600–1610 cm–1, and the vibrational characteristics of thiazole ring have been found at ~2600 cm–1. The bands assigned to the ν(C=N) is shifts to the lower frequency which indicates the involvement of nitrogen of Schiff base in chelation.

NMR Spectroscopy.

In addition to UV Vis and IR studies, some diamagnetic complexes and their ligands have been characterized by NMR spectroscopy. The Schiff bases exhibited signals due to all the expected protons in their expected region and have been found from the integration curve equivalent to the total number of protons deduced from the proposed structures these were compared with the reported sig nals of known comparable compounds and give further support for the compositions of the new ligands as well as their complexes. Comparison of chemical shift of uncomplexed Schiff bases with those of corresponding zinc complexes show that some of the resonance signals underwent a shift upon complexation. In each case proton assigned to aromatic and azomethine moieties were found at ~7.1–8.1 and 6.8 ppm in the spectra of Schiff bases. The protons due to azomethine and aromatic groups underwent a downfield shift of 0.9–1.0 ppm in the complexes indicating coordination of these groups with the metal ion. 13C NMR spectra likewise showed similar diagnostic features for the Schiff as well as their metal complexes.

X-Ray Diffraction

To obtain further evidence about the structure of metal complexes Xray diffraction was performed. The diffractro grams obtained for Schiff base metal complexes indicates crystalline nature for the complexes. It has been reported that the pattern of the Schiff base are differs from its metal complexes, which may be attributed to the formation of well-defined distorted crystalline structure. Probably this behavior is due to the incorporation of water molecules into the coordination sphere.

CONCLUSION:

Great efforts have been made to the incorporation of biomolecules into the synthesis of biologically po tent ligands and their metal complexes and to enable specific target. Aromatic Schiff bases or their metal chelates are being used to catalyze reactions on oxygenation, hydrolysis, electro reduction and decomposition. Complexes of thallium (I) with the benzothiaz olines show antibacterial activity against pathogenic bacteria. Various spectra data suggested that the thiazole complexes are good in biological as well as in the synthetic use.

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