PREPARATION AND STUDY OF SCHIFF BASE COMPLEXES WITH SOME TRANSITION METALS

A thesis
Submitted By

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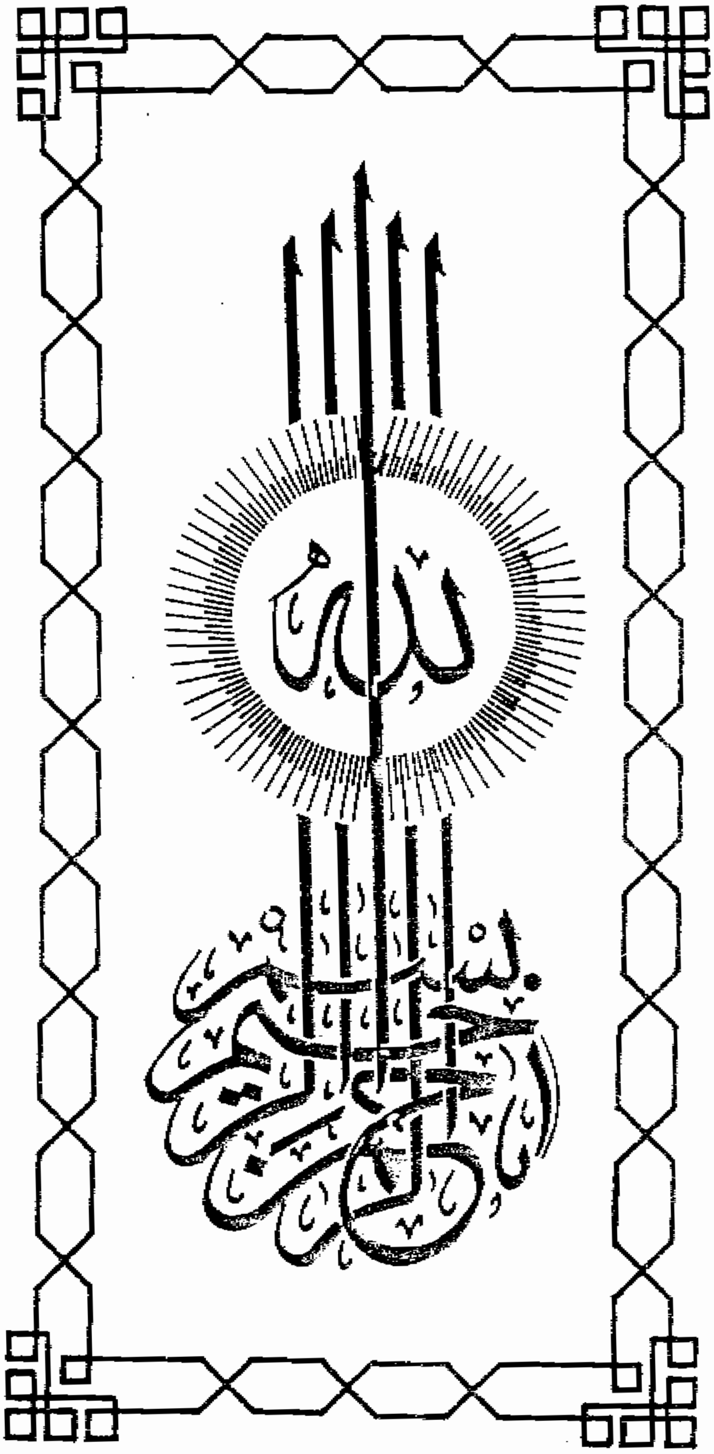
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Preparation and study of Schiff base complexes with some transition metals

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I am very glad to inform you that your paper entitled Mononuclear Cu(II) Oxamido Complex As A Chelating Agent for Some Transition.... is recommended for publication. The paper will be published in 9/94.

Prof. dr B. Baranowski
(Editor-in-chief)

lease, send us over
a discette with
ur paper (as soon as possible)

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CHAPTER 1

INTRODUCTION

I. IMPORTANCE OF TRANSITION METAL COMPLEXES OF SCHIFF BASE LIGANDS

Transition metals occur in metalloenzymes [1-7] bound to a macrocycle such as heme ring or to donor atoms of peptide chains usually in a distorted environment, as in hemerythin (Fe_2) [4,5] or hemocynin (Cu_2) [6,7].

Schiff base complexes have received considerable attention as biomimic model compounds [3,8-11]. Complexes of cobalt(II) involving derivatives of salicylaldehyde and aliphatic amines are similar to bilogical dioxygen carriers [11-19], as well as their potential as catalysts for the insertion of oxygen into organic substrates [20-22].

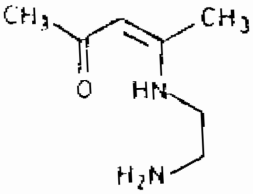
In particular, the dioxygen adduct of N,N′-ethylenebis(salicylideneiminato)cobalt(II), [Co(Salen)], of formula [Co(Salen)(O_2)L] and [{Co(Salen)L}$_2$(O_2)] [L = pyridine ,N,N-dimethylformamide (DMF) or dimethylsulphoxide (DMSO)] have received intensive investigation and have been recently reviewed [3,23,24]. [Fe(Salen)] has become attractive as the model compound of natural iron protein, hemerythin, which binds molecular oxygen reversibly [25]. [Cu(Salen)] is also a potential model compound of hemocyanin. N,N-bis(acetylacetone)ethylenediaminatocobalt(II), [Co(acacen)], has also been reported to bind molecular oxygen reversibly in N,N-dimethylformamide [8,26].

Schiff base complexes incorporating two similar or different metal ions are also of special interest. They are similar to those found in the living organisms, e.g., enzymes and proteins which develop their activity in the presence of two or more metal ions [27-29]. These complexes are also useful in catalysis [30].

II. PREPARATION AND IMPORTANCE OF HALF-UNIT SCHIFF BASE LIGANDS

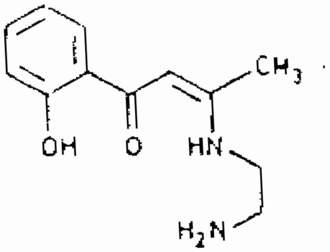
The condensation of diamines with ketonic compounds usually occur, in the molar ratio 1:2, to yield symmetrical Schiff base ligand such as acacen and salen.

Recently, chemists succeeded in preparing half-unit Schiff base compounds by reacting diamines with ketonic compounds, in the molar ratio 1:1, under specific conditions, e.g., using very dilute solutions, very slow addition of the diamine to the ketonic compound, continuous stirring during addition and thereafter for 18 hrs and finally separating the half-unit from the solvent under vacuum at relatively moderate temperature. Examples of the half-unit compounds are shown by Structure I [31] and Structure II [32].



I

Tridentate half-unit ligand



II

Tetradentate half-unit ligand

These half-unit compounds enabled the preparation of unsymmetrical Schiff bases by further condensing them with aldehydes and ketones.

III. LITERATURE SURVEY ON DIFFERENT TYPES OF SCHIFF BASE LIGANDS AND THEIR METALLIC COMPLEXES

The following survey on the different types of Schiff bases throw the light on the recent advances in this area. The examples selected here are more or less related to the Schiff base prepared in the present study.

(A) Bidentate Schiff Base Ligands

The bidentate Schiff base ligands N-R-salicylaldimines of the type NO-sites were prepared by the reaction