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Synthesis and Characterization of Transition Metal Complexes of Cu(II), Ni(II), Co(II) and VO(IV) with Tetradentate Ligands derived from substituted Acetophenone and Benzophenone

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ABSTRACT

Two tetradentate Schiff base ligands, N,N´-bis(2-hydroxy-5-methoxyacetophenone) ethylenediimine ($MaenH_2$) and N,N´-bis(2-hydroxy-4-methoxybenzophenone) ethylenediimine($MbenH_2$) were formed by 1:2 molar condensation of ethylenediamine with 2-hydroxy-5-methoxyacetophenone and 2-hydroxy-4-methoxybenzophenone respectively. These Schiff base ligands formed complexes (1:1 molar ratio) with Copper, Nickel, Cobalt and Oxovanadium ions. The complexes were characterized by Infrared, Electronic Spectra and elemental analysis. The spectra data of the ligands and their complexes were discussed based on the structural changes which occur due to complexation. The results suggest that the metal is bonded to the ligand through the phenolic oxygen and the imino nitrogen.

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Introduction

Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ion in the periodic table. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been discovered that many of these complexes may serve as model for biological important species as well as variety of application in biological clinical and analytical fields [1,2].

Schiff base complexes have been studied for their dioxygen uptake[3], oxidative catalysis[4] and potential catalysts for the insertion of oxygen into an organic substrate [5-7].

The reaction of tetradentate Schiff bases derived from salicylaldehyde and diamine has been the subject of many authors[8-12]. The present study aimed to investigate the reaction of two tetradentate Schiff bases derived from condensation of ethylenediamine with 2-hydroxy-5-methoxyacetophenone and 2-hydroxy-4-methoxybenzophenone with copper, nickel, cobalt and oxovanadium ions. The prepared ligand and complexes were characterized by elemental analysis, UV-visible as well as infrared spectroscopy.

Experimental

Materials

All the chemicals were reagent grade and used as commercially obtained (Aldrich, BDH) without further purification.

Analytical methods and physical measurement

Elemental analysis (C,H,N) for the ligands and complexes were carried out in Micro Analytical Laboratory of the Department of Chemistry, University of Manchester, U.K on Carlo Erba EA1108 Elemental Analysis.

The Infrared (IR) Spectra were recorded on a Pekin-Elmer infrared spectrophotometer with KBr pellets in range of (4000-250)cm^{-1} at the University of Zululand, South Africa. The UV-vis spectra (in chloroform) of the complexes were done in HEλIOB UV-visible spectrophotometer V4.55. The melting points were determined using liquid paraffin.

The percentage of Copper, Nickel and Cobalt contents in the complexes were determined by EDTA titration while that of vanadium was estimated gravimetrically.

Preparation of Ligands (Schiff bases)

The Schiff bases were prepared in 1:2 molar ratio condensation. A solution of 0.05 mole (3.005g) of ethylenediamine (dissolved in 25ml of ethanol) was slowly added to each solution of 0.1 mole (16.618g, 22.825g) of 2-hydroxy-5-methoxyacetophenone and of 2-hydroxy-4-methoxybenzophenone in (25 ml ethanol) respectively. After stirring the reaction mixture for an hour at 40-50°C, the precipitate was cooled, collected by filtration and washed several times with de-ionised water, then with ethanol and dried over anhydrous $CaCl_2$. Analytical data of ligands are presented in Table 1.

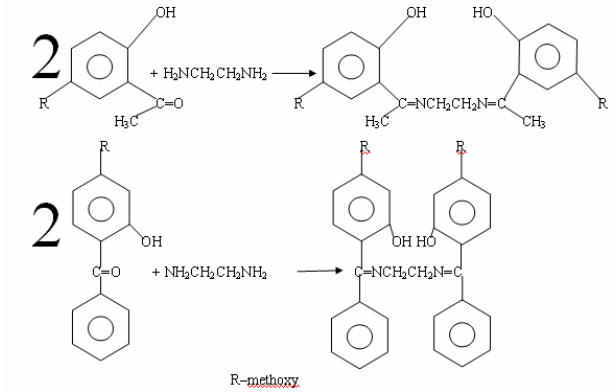

Fig. 1 : Structural representation of the Schiff bases (ligands)

Preparation of Complexes

Co(II) and Cu(II) complexes were prepared by the addition of 5mmole (0.498g or 1.2454g) of $Cu(CH_3COO)_2.H_2O$ or $Co(CH_3COO)_2.4H_2O$ which were dissolved in 20ml of de-ionized water, into a hot methanolic solution of 5mmole of the ligand. The mixture was then refluxed for an hour. The products

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formed were cooled, filtered and washed with methanol and dried over anhydrous calcium chloride.

Ni(II) and VO(IV) complexes were obtained in a similar way to the preparation of Co(II) and Cu(II) complexes described above. Ni(II) and VO(IV) were prepared by the addition of 5mmole $NiSO_4.6H_2O$ or $VOSO_4.H_2O$ (in 20ml de-ionised water) and 10mmole CH_3COONa (in 10ml de-ionised water), into hot methanol solution of 5mmole of the ligand. The products formed were washed free of sulphate with de-ionised water, then with methanol and dried over anhydrous Calcium chloride. Analytical data of the complexes are presented in Table 1.

The formation of the complexes may be represented by the general equation thus:

$$MX_2.nH_2O + QR\text{-}H_2 \xrightarrow[\text{de-ionised water}]{\text{methanol}} MQR.nH_2O + 2HX$$

$QR\text{-}H_2$ – dibasic tetradentate Schiff base.

Results and Discussion

The elemental analysis data of the Schiff bases and their complexes (given in Table 1) are consistent with the calculated results from the empirical formula of each compound. The elemental analyses also agreed well with 1:1 metal to ligand stoichiometry for all the complexes. The complexes are of various colours different from the colours of ligands indicating that the colours formed depend on the metal ions. The complexes are insoluble in water, sparingly soluble in ethanol and methanol and soluble in chloroform and DMF as shown in Table 2. The melting points of the complexes are different (higher) than that of the ligand, an evidence for complexation. The tetradentate N_2O_2 donor site of the ligands ($MaenH_2$ and $MbenH_2$) are capable of complexing various transition metal ions and in all complexes, the ligands bind through the oxygen of the phenoxyl group and nitrogen of the azomethine (C=N).

Infrared spectral

The important bands in the IR spectra of the Schiff base ligands ($MaenH_2$ and $MbenH_2$) as well as complexes are shown in Table 3.

Broad and weak ligands bands in the region 2833 – 2857cm^{-1} which has no corresponding bands in the metal complexes, and is assigned to intramolecular hydrogen-bonded OH[8-10]. A broad band around 3426 – 3566cm^{-1} in all complexes can be assigned to the O-H vibration of water of crystallization[11-12].

A strong band appeared at 1584cm^{-1} in $MaenH_2$ and 1614cm^{-1} in $MbenH_2$ and assigned to the C=N stretching vibration[10,13,14]. In complexes of $MaenH_2$, C=N bands are shifted by about 8-32cm^{-1} bathochromically while C=N bands are shifted hypsochromically by 5-21cm^{-1} in complexes of $MbenH_2$. This suggested the involvement of azomethine group (C=N) in the coordination with the metal ions and bonded through imino nitrogen atom[15,16].

The phenolic C-O stretching vibrations that appeared at 1250 and 1271cm^{-1} in the Schiff base ligands undergone shift towards higher frequencies (13-21cm^{-1}) in $MaenH_2$ complexes and towards lower frequencies (13-21cm^{-1}) in $MbenH_2$ complexes. The shift of the bands suggests the coordination of the phenolate anions with metal ions via deprotonation[17]. This shift confirms the participation of oxygen in the C-O-M bond[18,19]. The ring skeletal vibrations (C=C) were consistent in all derivatives and unaffected by complexation.

In low frequency region, the new absorption bands observed in the region 440 – 440cm^{-1} and 519 – 581cm^{-1} were attributed to v(M-phenolic-O) and v(M-N) respectively[19,20].

All the IR data suggest that the metal was bonded to the Schiff bases through the imino nitrogen and phenolic oxygen[19].

Electronic Spectra nm(cm^{-1})

The electronic spectra of Cu(II) complexes in chloroform consist of two bands in the range of 542-645nm(18,450 – 15, 504cm^{-1}) and 359 – 437nm (27,855 – 22, 883cm^{-1}) and these were assigned to $^2B_{1g} \longrightarrow {}^2A_{1g}$ and $^2B_{1g} \longrightarrow {}^2E_g$ respectively. The spectra pattern suggested a square planar geometry around the copper (II) ion[9].

The solution spectra data obtained for Co(II) complexes consist of band 396-464nm(25,253 – 21, 552cm^{-1}) and was assigned to $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$. The spectra of Ni(II) complex consists of two transition band 541-575nm(18,484 – 17,391cm^{-1}) and 416-464nm(24,038 – 21,552cm^{-1}) assigned to $^3T_1 \longrightarrow {}^3A_1$ and $^3T_1 \longrightarrow {}^3T_1(P)$ respectively. This is a probable indicative of four coordinate square planar geometry[9,21].

Band I and Band II were not observed for oxovanadium(IV) complex, only Band III was observed at 426nm(23,474cm^{-1}) and this may be either assigned to the $d_{xy} \longrightarrow dx^2\text{-}y^2$ ($^2B_2 \longrightarrow {}^2A_1$) transition or thought to be a low energy charge transfer band[11, 22, 23].

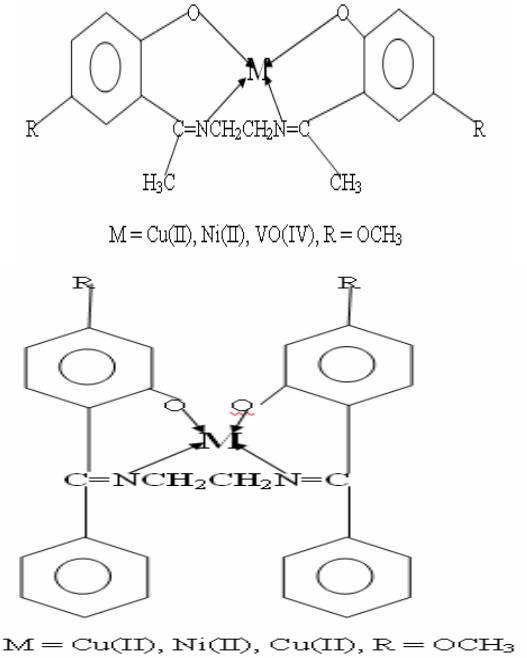

Figure 2: Proposed Structural Representation of Metal Complexes

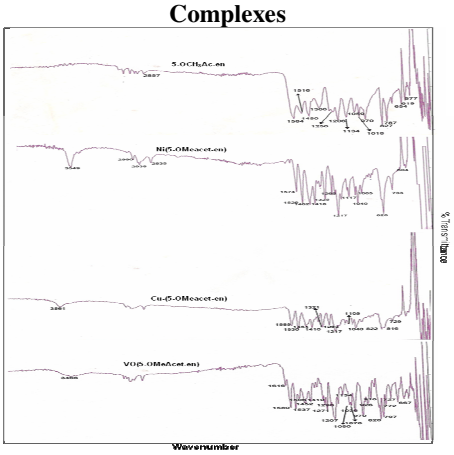

Fig 3A: IR Spectra of Ligand ($MaenH_2$) and its complexes

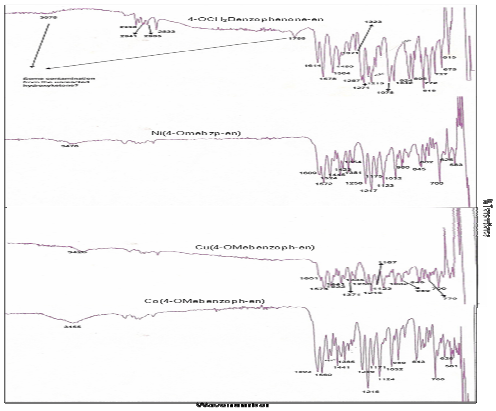

Fig 3B:IR spectra of ligand($MbenH_2$) and its complexes.

Conclusion

Six complexes of N,N´-bis(2-hydroxy-5 methoxyacetophenone)ethylenediimine and N,N´-bis(2-hydroxy-4-methoxybenzophonone)ethylenediimine were synthesized and isolated. They were characterized using Elemental analysis, IR and Electronic Spectroscopies. The Schiff base ligands act as tetradentate ligands and bonded to the metal ions through phenolic oxygen and imino nitrogen.

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Table 1: Analytical Data and some Physical Properties of Schiff bases (ligands) and their Complexes

	Formular	Molar Mass (g)	Colour	Yield %	Melting point °C	%C found (calcd)	%H Found (calcd)	%N found (calcd)	%M found (calcd)
$MaenH_2$	$C_{20}H_{24}O_4N_2$	356.43	Deep yellow	87.87	184-186	67.46 (67.40)	6.82 (6.79)	7.77 (7.86)	-
Maen-Cu	$C_{20}H_{23}O_{4.5}N_2$-Cu	426.96	Brown	98.40	> 205	56.78 (56.26)	5.42 (5.43)	6.59 (6.56)	14.74 (14.88)
Maen-Ni	$C_{20}H_{23}O_{4.5}N_2$-Ni	422.13	Brownish yellow	83.10	> 205	57.34 (56.90)	5.29 (5.49)	6.55 (6.64)	14.57 (13.91)
Maen-VO	$C_{20}H_{22}O_5N_2$-V	421.35	Green	71.60	> 205	56.24 (57.01)	5.47 (5.26)	6.68 (6.65)	11.30 (12.09)
$MbenH_2$	$C_{30}H_{28}O_4N_2$	480.57	Yellow	53.66	178- 180	74.79 (74.98)	5.60 (5.87)	5.54 (5.83)	-
Mben-Cu	$C_{30}H_{28}O_5N_2$-Cu	560.11	Purple	97.40	> 205	64.79 (64.33)	5.04 (5.03)	5.06 (5.00)	11.39 (11.34)
Mben-Ni	$C_{30}H_{26}O4N_2$-Ni	537.26	Brownish yellow	93.60	> 205	67.27 (67.07)	4.74 (4.88)	5.10 (5.21)	10.70 (10.93)
Mben-Co	$C_{30}H_{30}O_6N_2$-Co	573.52	Yellowish brown	87.10	> 205	62.41 (62.83)	4.88 (5.27)	4.57 (4.88)	11.18 (10.28)

Table 2 : Solubility Data Of The Complexes

COMPLEXES	ETHANOL		METHANOL		CHLOROFORM		TOLUENE		WATER		ACETONE		DMF	
	C	H	C	H	C	H	C	H	C	H	C	H	C	H
Maen-Cu	SS	S	S	S	S	S	SS	S	IS	IS	SS	S	S	S
Maen-Ni	SS	SS	SS	SS	S	S	S	S	SS	SS	SS	SS	SS	S
Maen-VO	SS	SS	SS	SS	S	S	SS	SS	IS	IS	SS	SS	S	S
Mben-Cu	SS	SS	SS	SS	S	S	S	SS	IS	IS	SS	S	S	S
Mben-Ni	SS	S	SS	SS	S	S	S	S	SS	SS	SS	SS	SS	S
Mben-Co	SS	S	SS	S	S	S	S	S	SS	SS	S	S	S	S

C – Cold, H – Hot, S – Soluble, SS – Sparingly Soluble, IS – Insoluble, DMF – Dimethylformamide

Table 3 : IR Spectra data of the ligands and their complexes

Ligands/ Complexes	v(H_2O) lattice water	v(C=N)	v(C=C)	v(phenolic C=O)	v(M-N)	v(M-O)
$MaenH_2$	-	1584	1516, 1450	1250	-	-
Maen-Cu	3561	1576	1530, 1464, 1410	1263	519	440
Maen-Ni	3549	1574	1526, 1462, 1418	1265	525	445
Maen-VO	3466	1616	1537, 1452, 1410	1271	523	440
$MbenH_2$	-	1614	1578, 1504, 1450	1271	-	-
Mben-Cu	3426	1601	1574, 1522, 1441	1250	579	-
Mben-Ni	3478	1609	1572, 1524, 1445	1258	583	490
Mben-Co	3455	1593	1560, 1492, 1441	1256	581	484

Table 4 : Electronic Spectra data of the complexes

Complexes	λ_{max}nm(λ_{max}cm^{-1}) in chloroform
Maen-Cu	645(15,504), 542(18,450), 437(22,883), 365(27,397), 359(27,855)
Mben-Cu	555(18,018), 398(25,126)
Mben-Co	404(21,552), 441(22,676), 396(25,253)
Maen-Ni	575(17,391), 464(21,552)
Mben-Ni	541(18,484), 433(23,095), 416(24,038)
Maen-VO	426(23,474)