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Syntheses and Characterization of Some Tetradentate Schiff-Base Complexes and Their Heteroleptic Analogues

A. A. OSOWOLE

Department of Chemistry,
University of Ibadan, Ibadan, Nigeria.

aderoju30@yahoo.com

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Abstract: VO(IV), Ni(II) and Cu(II) complexes of the asymmetric Schiff base [(HOC₆H₃(OCH₃)C(C₆H₅):N(CH₂CH₂)N:C(CH₃)CH:C(C₆H₅)OH)], and their heteroleptic analogues with triphenyl phosphine and 2,2'-bipyridine have been synthesized and characterized by elemental analyses, conductance, magnetic, infrared and electronic spectral measurements. The ligand is tetradentate coordinating *via* the imine N and enolic O atoms. The Ni(II) and Cu(II) complexes adopt a four coordinate square planar geometry, the VO(IV) complex is five coordinate square-pyramidal and the heteroleptic complexes are 6-coordinate, octahedral. The assignment of geometry is collaborated by magnetic moments and electronic spectra measurements. The compounds are non-electrolyte in nitromethane and are magnetically dilute.

Keywords: Asymmetric Schiff-base, Heteroleptic complexes, Magnetically dilute, Non-electrolyte, Tetragonal geometry.

Introduction

Metal complexes of Schiff bases are extensively studied due to synthetic flexibility, selectivity and sensitivity towards a variety of metal atoms¹. They are found useful in catalysis, in medicine as antibiotics and anti-inflammatory agents and in the industry as anticorrosion²⁻⁸. Literature is abundant on physico-chemical properties of various symmetrical Schiff bases and chelates with their pyridine, 2,2'-bipyridine and 1,10-phenanthroline adducts⁹⁻¹³, while comparatively little is known on asymmetric Schiff-base complexes and their heteroleptic analogs with triphenyl phosphine and 2,2'-bipyridine¹⁴⁻¹⁹. Consequently, my findings on the asymmetric Schiff-base ligand (derived from condensation of 1-phenyl-1,3-butanedione, ethylenediamine and 2-hydroxy-4-methoxy benzophenone), its VO(IV), Ni(II) and Cu(II) complexes and heteroleptic analogs with triphenyl phosphine and 2,2'-bipyridine are hereby presented. All these compounds with the ligand (Figure 1) are new, being reported for the first time.

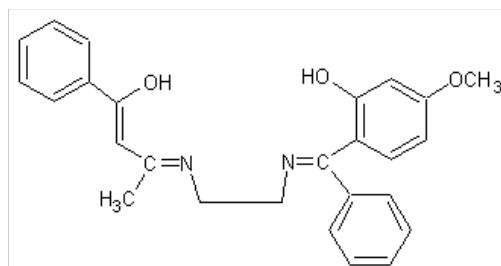


Figure 1. The structural formula the ligand

Experimental

Reagent grade 1-phenyl-1,3-butenedione, 2-hydroxy-4-methoxybenzophenone, ethylenediamine were obtained from Aldrich and used as received while vanadyl sulphate monohydrate, nickel(II) acetate tetrahydrate and copper(II) acetate monohydrate were available from BDH chemicals. Solvents were purified by standard methods²⁰.

The elemental analyses C, H and N were determined by Microanalytical Laboratory of Dipartimento di Scienze Chimiche, Universita di Trieste, Italy. Nickel and copper were determined titrimetrically and oxovanadium(IV) was estimated gravimetrically²¹. The IR spectra of the compounds were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer, as KBr discs in the range 4000 – 400cm⁻¹ while the solid reflectance spectra were measured on a Unicam Helios γ -spectrophotometer. Magnetic susceptibilities were measured on Johnson Matthey magnetic susceptibility balance and diamagnetic corrections were calculated using Pascal's constant²² while conductivity measurements were measured using a MC-1, Mark V conductivity meter with a cell constant of 1.0.

Syntheses

$[HO(C_6H_3(OCH_3)C(C_6H_5):N(CH_2)_2N:C(CH_3)CH:C(C_6H_5)OH)]$, (H_2L)

The ligand was prepared by modification of a literature method¹⁴. A mixture of 0.1 mol (6.00 g; 6.70 mL) ethylenediamine, 0.1 mol (22.83 g) 2-hydroxy-4-methoxybenzophenone and 0.1 mol (16.22 g) of benzoyl acetone, in 100 mL of ethanol was refluxed for two hours. The reaction mixture was cooled in ice and the yellow product, which was first formed, was filtered and washed with ethanol and dried over anhydrous calcium chloride.

Preparation of the metal complexes

The various complexes were prepared by addition of 5 mmol of Ni(CH₃COO)₂·4H₂O (1.24 g), Cu(CH₃COO)₂·H₂O (1.00 g) or VOSO₄·H₂O (0.82 g) in bits to a stirring 5 mmol of the ligand (2.21g) in 60 mL of dried methanol at room temperature (the Oxovanadyl mixture was buffered with 10 mmol of triethyl amine (1.08 g, 1.49 mL)). After stirring for thirty minutes, the resulting homogeneous solution of the complex was refluxed for 2 h and the precipitated solids were filtered, washed with methanol and dried over anhydrous calcium chloride.

Preparation of 2, 2'-bipyridine and triphenyl phosphine heteroleptic complexes

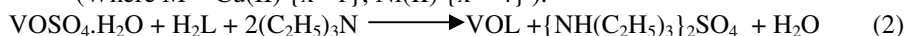
Triphenyl phosphine (1.30 g, 5 mmol) or 2,2'-bipyridine (0.79 g, 5 mmol) dissolved in 10 mL of ethanol was added slowly to a solution of the Schiff-base chelates, (2.50-2.54 g, 5 mmol) in 30 mL of ethanol while stirring. The mixture was refluxed for 1 h and the product formed was filtered, washed with ethanol several times and dried under vacuum.

Results and Discussion

The reactions of the various metal(II) Schiff bases and heteroleptic analogs can be represented by equations 1-3. The compounds are formed in moderate yields (30-80%). The general equation for the formation of the compounds is given below:



(Where M = Cu(II) {x = 1}; Ni(II) {x = 4}).



The reactions of the metal(II) Schiff bases with triphenyl phosphine/ 2, 2'-bipyridine in ethanol to give the heteroleptic complexes is as shown below:



(Where M = VO(IV), Ni(II), Cu(II) ; A = triphenyl phosphine/ 2, 2'-bipyridine).

The C, H and N data, percentage yields and melting points are presented in Table 1. The molar conductances of the compounds that dissolved in nitromethane were below $15.00 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ indicating that they were non-electrolytes, since a value in the range $75-90 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ is expected for a 1:1 electrolyte.

Table 1 Analytical Data for Compounds.

Compound (Empirical formula)	Formula weight	%Yield	M.pt °C	Anal. found (Cal) %				\wedge_m Ωcm^2 mol^{-1}	μ_{eff} (B.M)
				C	H	N	M		
H ₂ L (C ₂₆ H ₂₆ N ₂ O ₃)	442.76	70	138-139	70.50 (70.53)	5.92 (5.92)	6.34 (6.33)	-	-	-
[VOL] (VO(C ₂₆ H ₂₄ N ₂ O ₃))	507.68	80	234-236	61.50 (61.51)	4.79 (4.77)	5.54 (5.52)	10.02 (10.03)	14.00	1.74
[VOL(P(Ph) ₃)] (VO(C ₄₄ H ₃₉ N ₂ O ₃ P))	769.97	60	211-213	68.62 (68.64)	5.00 (5.01)	3.62 (3.64)	6.67 (6.62)	12.00	1.75
[VOL(bipy)] (VO(C ₃₆ H ₃₂ N ₄ O ₃))	663.87	60	236-238	65.11 (65.13)	4.80 (4.82)	8.42 (8.44)	7.66 (7.67)	10.00	1.76
[NiL] (Ni(C ₂₆ H ₂₄ N ₂ O ₃))	499.45	80	205-206	62.50 (62.53)	4.83 (4.84)	5.60 (5.61)	11.80 (11.75)	12.00	0
[NiL(P(Ph) ₃) H ₂ O] (Ni(C ₄₄ H ₄₁ N ₂ O ₄ P))	779.76	50	210-211	67.75 (67.78)	5.32 (5.30)	3.60 (3.59)	7.56 (7.53)	11.00	3.20
[NiL(bipy)] (Ni(C ₃₆ H ₃₂ N ₄ O ₃))	655.64	30	230-231	65.93 (65.95)	4.86 (4.88)	8.56 (8.55)	8.98 (8.96)	9.00	3.27
[CuL] (Cu(C ₂₆ H ₂₄ N ₂ O ₃))	504.29	80	240-242	61.94 (61.93)	4.79 (4.80)	5.57 (5.56)	12.80 (12.60)	13.12	1.98
[CuL(P(Ph) ₃) H ₂ O] (Cu(C ₄₄ H ₄₁ N ₂ O ₄ P))	784.60	60	220-221	67.34 (67.36)	5.30 (5.27)	3.57 (3.57)	10.00 (10.05)	11.00	2.03
[CuL(bipy)] (Cu(C ₃₆ H ₃₂ N ₄ O ₃))	660.48	60	238-239	65.60 (65.50)	4.85 (4.84)	8.46 (8.48)	9.62 (9.61)	10.00	2.07

Spectral study

The ultraviolet spectra of the compounds are characterized by two peaks between 29.00-35.00 and 40.00-50.00 kK respectively, assigned to $\pi-\pi^*$ transitions (of various origin) and charge transfer transition respectively¹⁴⁻¹⁶. The oxovanadium(IV) complex, electronic spectrum shows three absorption bands at 15.45, 17.55 and 26.50 kK respectively, which is consistent with a five-coordinate, square-pyramidal geometry and is assigned to $b_{2 \rightarrow} e^*_{\pi}$ (band I), $b_{2 \rightarrow} b_1$ (band II) and

$b_2 \rightarrow a_1$ (band III) transitions. The heteroleptic analogs, on the other hand display one to two bands at 14.05 and 18.35-19.00 kK which is indicative of a six-coordinate tetragonal (octahedral) geometry²⁴. The Ni(II) complex has two absorption bands at 18.05 and 22.70 kK, typical of a 4-coordinate square planar geometry and is assigned to $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1A_{2g}$ transitions. The heteroleptic complexes, however, have three absorption bands between 18.10-18.25, 22.42-23.00 and 24.04-24.89kK respectively, assigned to $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ (ν_3) transitions of a six-coordinate octahedral geometry¹⁴⁻¹⁵.

The copper(II) complex studied, displays two bands at 18.05 and 23.81 kK, assigned to $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2E_{1g}$ transitions of 4-coordinate square planar geometry while the heteroleptic analogs have an unsymmetrical band around 17.69 kK which is indicative of a six-coordinate tetragonal (octahedral) arrangement of the ligands around the copper ion²⁴.

Infrared Spectra

The strong band at 3300 cm^{-1} , which is conspicuously absent in the spectra of the complexes, is assigned as νOH stretching frequency in the ligand, which indicates deprotonation and involvement of the enol O in chelation. The uncoordinated C=N and C=C stretching vibrations occur as coupled bands expectedly in the ligand at $1606\text{-}1542\text{ cm}^{-1}$ and are bathochromic shifted to $1600\text{-}1513\text{ cm}^{-1}$ on coordination to the metal ions¹⁸⁻¹⁹, indicative of the involvement of N and O donor atoms of C=N and enol groups respectively, in coordination to the metal ions. In heteroleptic complexes, these bands are hypsochromic shifted to $1608\text{-}1516\text{ cm}^{-1}$ which is indicative of a stronger M-P/M-N (base) bonds in them¹⁹. The $\nu(\text{V}=\text{O})$ bands appeared very strong between $940\text{-}980\text{ cm}^{-1}$ while those due to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})/\nu(\text{M}-\text{P})$ were observed¹⁴⁻¹⁵ at $494\text{-}444$ and $599\text{-}525\text{ cm}^{-1}$ (Table 2).

Table 2. Infrared and Electronic Spectral Data of the Complexes.

Compound	νOH	$\nu(\text{C}=\text{N})$ + $\nu(\text{C}=\text{C})$	$\nu(\text{M}-\text{N})/\nu(\text{M}-\text{P})$	$\nu(\text{M}-\text{O})$	$\lambda\text{ max (kK)}$
H_2L	3300s	1606s 1542s	-	-	29.00 35.00 42.00 49.00
[VOL]	-	1583s 1519s	525s	444s	15.45 17.55 26.50 33.30 41.00
[VOL(P(Ph) ₃)]	-	1600s 1581s	542s	494s	14.05 18.35 32.00 40.00
[VOL(bipy)]	-	1601s 1582s	559s	465m	19.00 31.00 40.00
[NiL]	-	1600s 1513s	595s	473s	18.05 22.70 30.00 41.00
[NiL(P(Ph) ₃)H ₂ O]	3500b	1608s 1518s	599m	484s	18.10 23.00 24.04 34.00 41.00
[NiL(bipy)]	-	1608s 1516s	559m	483m	18.25 22.42 24.89 34.00 41.00
[CuL]	-	1577s 1513s	595s	468s	18.05 23.81 34.00 41.00
[CuL(P(Ph) ₃)H ₂ O]	3500b	1589s 1516s	582m	451s	17.19 31.00 41.0
[CuL(bipy)]	-	1590s 1517s	595m	473m	18.18 30.00 40.00

b = broad, m = medium, s = strong, 1kK = 1000 cm^{-1}

Magnetic Moments

Oxovanadium(IV) complexes are expected to have a moment of 1.73B.M, regardless of the geometry, when the orbital contribution is completely quenched by low symmetry fields. However, in the compounds studied a moment in the range 1.74-1.76 B.M is observed, indicative of monomeric compounds. In the Ni(II) compounds reported in this work, the complex is diamagnetic while the heteroleptic complexes have moment of 3.20 and 3.27 B.M, respectively. The former is indicative of a four coordinate, square planar geometry while the latter is suggestive of a six coordinate, octahedral geometry²². The magnetic moments of 1.98 - 2.07 B.M. is observed for the copper(II) compounds, which indicate that they are magnetically dilute and are higher than the spin-only value of 1.73 B.M. as a result of orbital contribution and spin-orbit coupling²².

Conclusion

The asymmetric Schiff-base ligand coordinates to the VO(IV), Ni(II) and Cu(II) ions in a tetradentate manner using the azomethine N and enol O atoms. The assignment of a 4-coordinate, square planar for Ni and Cu complexes, a 5-coordinate square-pyramidal geometry for the VO(IV) complex and 6-coordinate octahedral geometry (Figure 2) for their heteroleptic analogs is corroborated by magnetic, infrared and electronic spectral measurements.

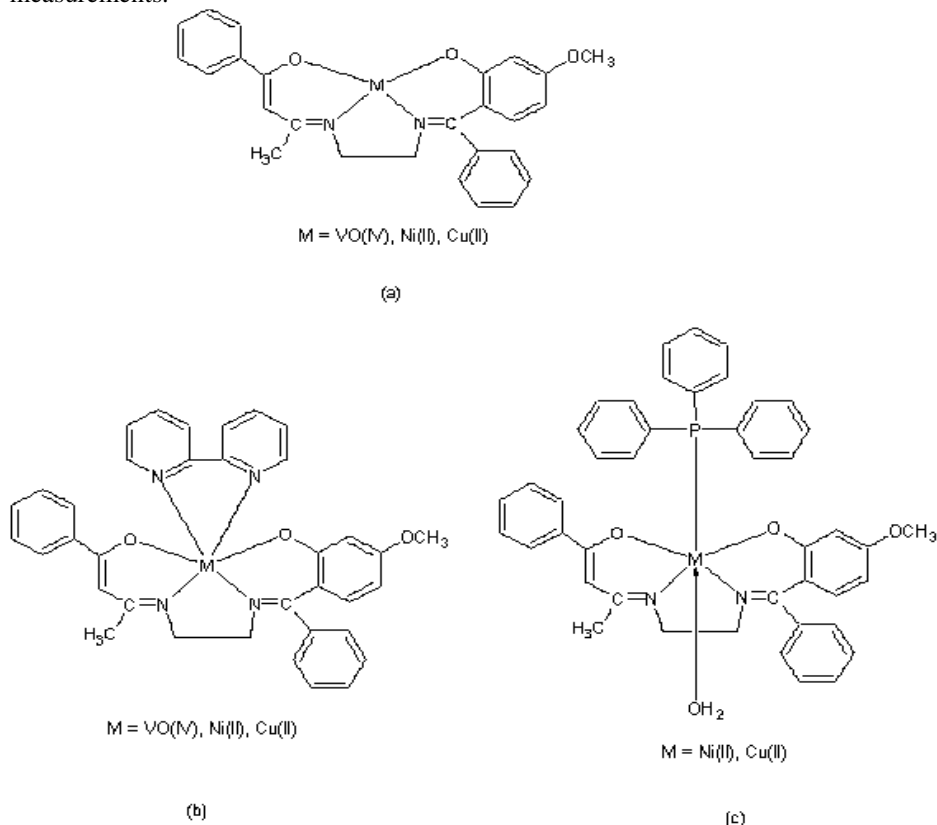


Figure 2. The proposed coordination spheres of the Schiff-base Complexes (a) and their heteroleptic analogs (b and c).

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