STUDIES ON SOME VO(IV), Ni(II) AND Cu(II) COMPLEXES OF NON-SYMMETRICAL TETRADENTATE SCHIFF-BASES

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ABSTRACT. The coordination chemistry of VO(IV), Ni(II) and Cu(II) with unsymmetrical Schiff base ligands, $[HO(OCH_3)C_6H_3C(CH_3):N(CH_2CH_2)N:C(CH_3)CH:C(C_6H_5)OH]$, H_2L and $[HO(OCH_3)C_6H_3C(CH_3):N(CH_2CH_2)N:C(CH_3)CH:C(CH_3)OH]$, H_2L^1 (derived from condensation of 1-phenyl-1,3-butanedione/2,4-pentanedione, ethylenediamine and 5-methoxy-2-hydroxy acetophenone) is discussed. The metal complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility, infrared and electronic spectral measurements. They are magnetically dilute, non-electrolytes in nitromethane. The ligands are tetradentately coordinating via the imine N and enolic O atoms, resulting in 5-coordinate square-pyramidal geometry for the VO(IV) complexes and 4-coordinate square-planar geometry for the Ni(II) and Cu(II) complexes. The assignment of geometry is supported by magnetic and spectral measurements.

KEY WORDS: Coordination chemistry, Magnetically dilute, Non-electrolyte, Non-symmetrical Schiff base

INTRODUCTION

Schiff bases and its metal chelates have played important roles in the development of chemical industries through catalysis, substrate carriers and dyes [1-6]. Tucareso, a Schiff base-forming immunomodulator, is currently undergoing pilot phase I/II clinical trials as an immunopotentiator in chronic hepatitis B virus infection, HIV infection and malignant melanoma [7]. These ligands are widely studied because of their pronounced coordinating properties and stability [8-9]. A number of symmetrical Schiff bases and chelates have been reported [1-15], while comparatively little is known on synthesis and physico-chemical properties of asymmetric Schiff-base ligands and metal complexes [16-20]. Consequently, the aim of this work is to synthesize and characterize unsymmetrical Schiff-base ligands (derived from condensation of 1-phenyl-1,3-butanedione/2,4-pentanedione, ethylenediamine and 5-methoxy-2-hydroxy acetophenone) and their VO(IV), Ni(II) and Cu(II) complexes, in order to see the effect of the mixed π-electron ligand system and phenyl/methyl substituent on geometries and physico-chemical properties. The choice of oxovanadium(IV) and Cu(II) is based on the Jahn-Teller effect, normally associated with them while Ni(II) is chosen to investigate the possibility of equilibrium between its square planar and tetrahedral forms. The ligands used for this study, with the acronym H_2L and H_2L^1, are new with their metal complexes, being reported here for the first time.

EXPERIMENTAL

Reagents and Solvents

Reagent grade 2,4-pentanedione, 1-phenyl-1,3-butanedione, 5-methoxy-2-hydroxy-acetophenone, ethylenediamine, were obtained from Aldrich and used as received while vanadyl sulfate monohydrate, nickel(II) acetate tetrahydrate and copper(II) acetate monohydrate were available from BDH Chemicals. Solvents were purified by standard methods [21].

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Preparation of the ligands

Preparation of [OH(OCH₃)C₆H₃C(CH₃):N(CH₂)₂N:C(CH₃)CH:C(C₆H₅)OH)], H₂L. Ethylenediamine 0.1 mol (6.00 g; 6.70 mL) in 20 mL of dried ethanol was added dropwise to a stirring ethanolic solution (80 mL) of 0.1 mol (16.62 g; 12.05 mL) 5-methoxy-2-hydroxy acetophenone and 0.1 mol (16.22 g) of benzoyl acetone. The resulting homogeneous mixture was refluxed for 2 h and left overnight at room temperature. The yellow product, which was first formed, was filtered and washed consecutively with ethanol and ether. It was dried over anhydrous calcium chloride and recrystallized from hot ethanol to give the required Schiff base. The yield of the title compound was 24.67 g (70 %). The same procedure was used to prepare and isolate [OH(OCH₃)C₆H₃C(CH₃):N(CH₂)₂N:C(CH₃)CH:C(CH₃)OH)], H₂L[1], (yield 17.42 g, 60 %).

Preparation of the metal(II) complexes, [ML]
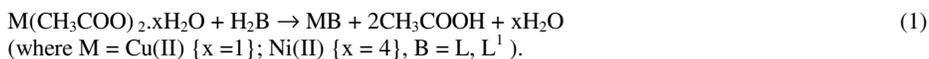
To the ligand, 5 mmol (1.76 g) stirred in 50 mL of methanol, was added in small portions 5 mmol of Ni(CH₃COO)₂.4H₂O (1.24 g), Cu(CH₃COO)₂.H₂O (1.00 g) or VOSO₄.H₂O (0.82 g). The color of the reaction mixture changed after a few minutes and was refluxed for 2 h. The precipitated solid formed on cooling was filtered, washed with ethanol and dried over anhydrous calcium chloride. The same procedure was used to prepare and isolate the ML[1] complexes.

Physical measurements

The infrared spectra of complexes were measured as KBr discs on a Perkin-Elmer FTIR Paragon 1000 spectrometer in the range 4000-400 cm^{-1} while the electronic spectra in chloroform were recorded on a Perkin-Elmer λ20 spectrophotometer. The elemental analyses (C, H and N) were determined by the Microanalytical Laboratory of Dipartimento di Scienze Chimiche, Universita di Trieste, Italy. Nickel and copper were determined titrimetrically while oxovanadium(IV) was estimated gravimetrically [22]. Magnetic susceptibilities were measured on a Johnson Matthey magnetic susceptibility balance and diamagnetic corrections were calculated using Pascal's constants [23]. Melting points (uncorrected) were determined using a Stuart scientific melting point SMP1 machine. Electrolytic conductivities of the soluble compounds in nitromethane at 25 °C were determined using a MC-1, Mark V conductivity meter with a cell constant of 1.0. Single crystal X-ray structural measurements could not be taken on any of the complexes because no good crystals were obtained.

RESULTS AND DISCUSSION

The reactions for the formation of the various metal(II) Schiff base complexes are represented by equations 1 and 2. The compounds are formed in moderate yields (30-80 %).

$$M(CH_3COO)_2.xH_2O + H_2B \rightarrow MB + 2CH_3COOH + xH_2O \qquad (1)$$
(where M = Cu(II) {x =1}; Ni(II) {x = 4}, B = L, L[1]).

$$VOSO_4.H_2O + H_2B \rightarrow VOB + H_2SO_4 + H_2O \qquad (2)$$
(where B = L, L[1]).

The structural formula of the ligands is shown in Figure 1. The formations of these ligands are confirmed by microanalysis. The alternative formations of aliphatic Schiff bases arising from the condensations of 2,4-pentanedione/1-phenyl-1,3-butanedione and ethylenediamine is ruled out, since these products have been previously reported as straw and white-coloured, with melting points of 111-112 and 180.5 °C, respectively [24, 25]. Consequently, the formation of the unsymmetrical analogues could be distinguished from the symmetrical bis(5-methoxy-2-

hydroxy acetophenone)ethylenediimine by microanalytical data, since they have different molar masses. The microanalyses support the predominant formation of the unsymmetrical Schiff bases. The colors, percentage yields, molar conductances, analytical data and melting points of the complexes are presented in Table 1.
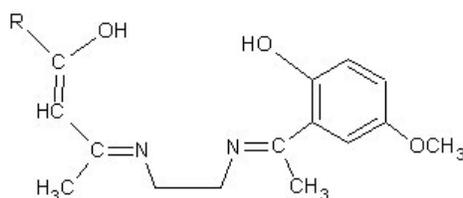

Figure 1. The structures for the ligands (H_2L, R = C_6H_5; H_2L^1, R = CH_3).

Table 1. Analytical data for compounds.

Compound (emperical formula)	Formula weight	Color	Yield %	M.p. (°C)	% Analysis found (calc.)				Λm Ω^{-1} cm^2 mol^{-1}	μ_{eff} (B.M)
					C	H	N	M		
H_2L ($C_{21}H_{24}N_2O_3$)	352.44	Yellow	70	146-148	71.58 (71.57)	6.85 (6.86)	7.95 (7.95)	-	-	-
[VOL] VO($C_{21}H_{22}N_2O_3$)	417.36	Green	70	137-138	60.42 (60.44)	5.30 (5.31)	6.71 (6.71)	12.20 (12.21)	11.00	1.74
[NiL] (Ni($C_{21}H_{22}N_2O_3$)	409.13	Yellow	70	230-232	61.66 (61.65)	5.40 (5.42)	6.85 (6.85)	14.34 (14.35)	11.00	0
[CuL] (Cu($C_{21}H_{22}N_2O_3$)	413.97	Brown	70	200-203	60.94 (60.93)	5.35 (5.36)	6.77 (6.77)	15.33 (15.35)	13.00	1.93
H_2L^1 ($C_{16}H_{22}N_2O_3$)	290.37	Yellow	60	144-146	66.18 (66.19)	7.63 (7.64)	9.64 (9.65)	-	-	-
[VOL^1] (VO($C_{16}H_{20}N_2O_3$)	355.29	Light green	50	148-149	54.08 (54.09)	5.67 (5.67)	7.85 (7.89)	14.32 (14.34)	12.00	1.75
[NiL^1] (Ni($C_{16}H_{20}N_2O_3$)	347.06	Orange	50	220-222	55.36 (55.37)	5.82 (5.81)	8.06 (8.07)	16.90 (16.92)	11.00	0
[CuL^1] (Cu($C_{16}H_{20}N_2O_3$)	351.90	Brown	50	252-254	54.60 (54.61)	5.73 (5.73)	7.96 (7.96)	18.07 (18.06)	13.00	1.92

Molar conductances

The molar conductances of the metal complexes in nitromethane were observed below 14.00 ohm^{-1} cm^2 mol^{-1} showing that they were non-electrolytes. A value of 60-115 ohm^{-1} cm^2 mol^{-1} is expected for a 1:1 electrolyte.

Electronic spectra

The ultraviolet region of the electronic spectrum (Table 2) is characterized by π-π* and charge transfer transitions of the ligand, both in the free and in the coordinated forms at 28.00-34.00, 40.00-44.00 and 44.40-49.00 kK (ε, 2 - 60 x 10^3 M^{-1}cm^{-1}) [24].

The electronic spectra of the oxovanadium(IV) complexes, show two or three absorption bands at 13.00-14.20, 17.40-19.76 and 23.04 kK, respectively, typical of a five-coordinate, square-pyramidal geometry and the bands are 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, respectively [26].

Nickel(II) complexes are known to have a range of coordination numbers from six (octahedral) to four (square planar/tetrahedral). Their electronic spectra are typically characterized by the existence of complicated equilibria involving these different structural types [26]. However, the spectra of the Ni(II) complexes studied here, show two absorption bands around 17.60 and 23.68 kK, respectively, typical of a 4-coordinate square planar geometry and are assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions [19]. The absence of a band at 16.00 kK, $^3T_1(F) \rightarrow {}^3T_1(P)$, in the spectra of these complexes, implies the absence of tetrahedral forms of these complexes.

The assignments of Cu(II) complexes d-d transitions is more complicated because of the relatively low symmetry environment (*i.e.* less than cubic), in which the Cu(II) ion is characteristically found. However, in the cubic environment, the d^9 configuration makes the Cu(II) ion subject to Jahn-Teller distortions, giving rise to an unsymmetrical band. Regular tetrahedral compounds of copper(II) are not very common, but they usually have a single broad band of $\sim 10^2$ molar intensity below 10.0 kK with the spectra being blank between 10.0-20.0 kK, while square planar complexes absorb in the latter region [17, 26]. The copper(II) complexes synthesized in this study have two bands around 18.13 and 23.49 kK, assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_{1g}$ transitions of 4-coordinate, square planar geometry.

The molar absorptivities of (ε, 10^2-10^3 M^{-1}cm^{-1}) for Cu(II) and Ni(II) complexes and (ε, 30-40 M^{-1}cm^{-1}) for the VO(IV) complexes, are corroborative of square planar and square pyramidal geometries. However, band three in [VOL^1] at 23.04 kK (ε, 10^3 M^{-1}cm^{-1}) is higher than expected and this increase has been attributed to tailing of charge transfer bands from the UV region [9].

The change of a phenyl group to a methyl group does not have any significant effect on the geometry of the metal chelates (MB), since there is only a slight change in molar absorptivities (ε) values.

Table 2. Electronic spectra for the complexes (kK).

Compounds	d-d transitions (ε M^{-1}cm^{-1})	C.T./ π-π* transitions (ε x 10^3 M^{-1}cm^{-1})
H$_2$L	-	29.0 (20), 44.00 (20), 49.00(20) sh
[VOL]	13.00 (40), 17.40 (70)	28.00 (20), 33.00 (30), 40.00 (30)
[NiL]	17.60 (100), 24.00 (1000)	30.00 (2), 40.00 (10)
[CuL]	18.20 (400), 23.50 (1000)	29.00 (30), 32.00 (30), 41.00 (40)
H$_2$L^1	-	28.00 (20), 32.00 (8), 40.00 (5), 44.40 (10)
[VOL^1]	14.29 (30), 19.76 (30), 23.04 (1000)	25.06 (10), 32.26 (30), 40.32 (30)
[NiL^1]	17.50 (100), 23.35 (1000)	31.00 (60), 40.00 (50)
[CuL^1]	18.05 (500), 23.48 (1000)	25.00 (10), 33.00 (10), 41.00 (30)

Sh = shoulder.

Infrared spectra

The assignments of the infrared bands (Table 3) were made by comparing the spectra of the compounds with reported literature values on similar systems [16-20]. The strong bands at 3417-3375 cm^{-1} are assigned to a ν(OH) stretching frequency in the ligands and are conspicuously absent in the spectra of the complexes, indicative of deprotonation and involvement of the enol O in chelation. The uncoordinated C=N and C=C stretching vibrations occur as coupled bands at 1612-1570 cm^{-1}, in the ligands [19-20] which eventually underwent a bathochromic shift to 1606-1513 cm^{-1} on coordination to the metal ions. This is indicative of the involvement of N donor atoms of C=N, in coordination to the metal ions. The ν(V=O) band in the oxovanadyl compounds appeared as a very strong band at 940 and 961 cm^{-1} for [VOL^1] and [VOL], respectively. The strong bands, which are very prominent at 949-724 cm^{-1}, are attributed to δ(C-H) bands of phenyl rings. The M-N and M-O bands are observed at 599-502 and 474-429 cm^{-1}, respectively, confirming coordination through the imine N and enol O atoms [18-20].

Table 3. Relevant infrared spectral data of the complexes.

Compound	ν(OH)	ν(V=O)	ν(C=N)+ν(C=C)	δ (C-H)	ν(M-N)	ν(M-O)
H$_2$L	3375 s	-	1608 s, 1582 s	910 s, 776 s	-	-
[VOL]	-	961 vs	1603 s, 1543 s	829 s, 756 s	568 s, 531 s	474 s
[NiL]	-	-	1593 s, 1571 s	866 m, 746 s	578 s, 505 s	458 s
[CuL]	-	-	1592 s, 1515 s	936 s, 740 s	595 s, 531 s	468 s
H$_2$L^1	3417 s	-	1612 s, 1570 s	949 m, 766 s	-	-
[VOL^1]	-	940 vs	1606 s, 1515 s	895 s, 760 s	599 s, 528 s	470 m
[NiL^1]	-	-	1571 s, 1513 s	817 s, 724 s	575 s, 502 s	450 m
[CuL^1]	-	-	1586 s, 1532 s	946 s, 732 s	595 s, 540 s	429 m

Key: b = broad, m = medium, vs = very strong.

Magnetic moments

Oxovanadium(IV) complexes are expected to have a moment of 1.73 B.M. irregardless of the geometry, when the orbital contribution is completely quenched by low symmetry fields. However, in the complexes studied, a moment in the range 1.74-1.75 B.M was observed, indicative of monomeric compounds [23].

The magnetic moment of coordination compounds of Ni(II) in a cubic field fall between 2.8-4.2 B.M. while tetrahedral complexes have moments in the range 3.20-4.10 B.M. and square-planar complexes are diamagnetic [23]. The Ni(II) complexes reported in this work, are diamagnetic and consequently, four coordinate, square planar in geometry [19-20, 23], ruling out the presence of paramagnetic, tetrahedral forms.

The room temperature magnetic moments of the copper(II) compounds are expected to be higher than the spin-only value of 1.73 B.M. as a result of an orbital contribution and spin-orbit coupling, which mixes in the higher T terms into the ground term. Consequently, a moment of 1.90-2.20 B.M. is usually observed for mononuclear copper(II) complexes, regardless of stereochemistry [23]. Magnetic moments of 1.92 and 1.93 B.M. are observed for the copper(II) compounds, which indicate that they are magnetically dilute.

CONCLUSIONS

The non-symmetric Schiff-base ligands coordinate to the VO(IV), Ni(II) and Cu(II) ions in a tetradentate manner using the azomethine N and enol O atoms. The change of substituent from phenyl group in H$_2$L to CH$_3$ group in H$_2$L^1 does not have any significant effect on magnetic moments and geometries of the complexes. The Ni(II) complexes are diamagnetic while the VO(IV) and Cu(II) complexes are paramagnetic. The assignment of a 4-coordinate, square geometry for Ni(II) and Cu(II) complexes and a 5-coordinate, square-pyramidal geometry for the VO(IV) complexes is corroborated by magnetic, infrared and electronic spectral measurements (Figures 2).
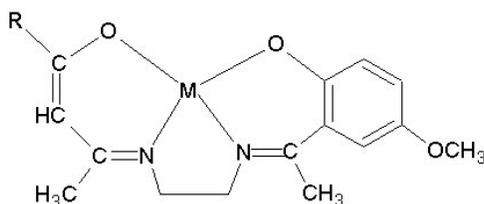

Figure 2. The structure for the metal(II) Schiff base complexes (M = VO, Ni and Cu).

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