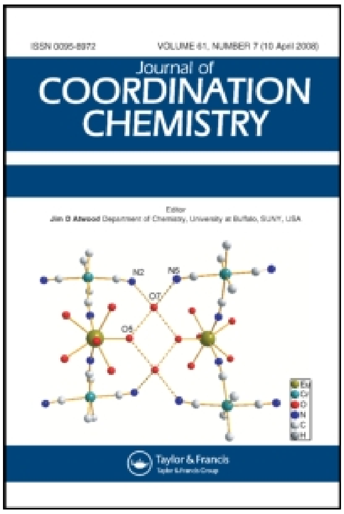

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Kolawole, Gabriel A. and Osowole, Aderoju A.(2009) 'Synthesis and characterization of some metal(II) complexes of isomeric unsymmetrical Schiff bases and their adducts with triphenylphosphine', Journal of Coordination Chemistry, 62: 9, 1437 — 1448

To link to this Article: DOI: 10.1080/00958970802621512

URL: http://dx.doi.org/10.1080/00958970802621512

Journal of Coordination Chemistry
Vol. 62, No. 9, 10 May 2009, 1437–1448

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Synthesis and characterization of some metal(II) complexes of isomeric unsymmetrical Schiff bases and their adducts with triphenylphosphine

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(*Received 12 May 2008; in final form 1 August 2008*)

We report the isolation of two unsymmetrical isomeric Schiff bases obtained from condensation of 2,4-pentanedione/1-phenyl-1,3-butanedione and 2-hydroxy-4-methoxyacetophenone/2-hydroxy-4-methoxybenzophenone with ethylenediamine and their VO(IV), Co(II), Ni(II), and Cu(II) complexes. Further reaction of each complex with triphenylphosphine resulted in formation of 1 : 1 adducts, with water occupying the sixth position in some, except copper and cobalt formed 1 : 2 adducts with [ML^1]. The purities of the ligands and complexes were established by microanalyses and the complexes were characterized by magnetic susceptibility, conductance, infrared and electronic spectral measurements. The involvement of the azomethine N and phenolic O in bonding resulted in an N_2O_2 chromophore around the central metal atom. Infrared and electronic spectral data are consistent with square-planar/tetrahedral geometry for Ni(II), Co(II), and Cu(II) complexes and a five-coordinate, square-pyramidal geometry for the VO(IV) complexes. Evidence for triphenylphosphine adducts is adduced from microanalyses, spectral changes, and magnetic susceptibility measurements.

Keywords: Adducts; Unsymmetrical Schiff base; Triphenylphosphine; Metal(II)

1. Introduction

The use of Schiff bases as ligands has enjoyed a very rich history with importance of metal complexes in a variety of industrial and biological applications. Stereochemical flexibility is well documented among Schiff-base complexes arising from central metal, the source of the carbonyl function, the amine, as well as substituents on and steric bulkiness around the Schiff base. Interest in tetradentate Schiff-base complexes involving symmetrical and unsymmetrical ligands is generated from potential uses in cancer treatment [1–3] as antimicrobial agents [4–9] in catalysis [10–14] as antiviral agents [3], in ability for dioxygen uptake [15–17] in materials [18] and as biological models [19, 20]. Recently, oxovanadium(IV) complexes of Schiff bases were used as catalysts in aerobic selective oxidation of olefin and cyclohexene, sulphide oxidation when bound to a resin or encapsulated in zeolite-Y [21–23], and in electrocatalysis and

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802621512

the determination of nitrite [24]. The insulin-enhancing properties of some Schiff-base complexes of VO(IV) [15, 25] and M(II) [26] complexes have also been reported. Some applications of Schiff-base complexes have been due to the ability to exhibit structural switches, e.g. Ni(II) or Cu(II), that can switch from square planar to tetrahedral either as ligand substitution changes or when put in solution. This also generates, particularly in the case on Ni(II), magnetic behaviors that are unique. Four-coordinate Ni(II) complexes adopt diamagnetic or paramagnetic behavior depending on whether they are square planar or tetrahedral. One unique characteristic of Schiff-base complexes of some VO(IV) complexes is from the ability of V(IV) to undergo reversible electron transfer [17].

Recently, we have focused our attention on symmetrical and unsymmetrical Schiff-base complexes of transition metals and the complexes formed by reacting these complexes with heterocyclic aromatic bases like 2,2′-bipyridine and 1,10-phenanthroline [27, 28] and, recently, with triphenylphosphine [29]. Literature is abundant on metal(II) complexes of various symmetrical Schiff bases, ketoamines/ketoimines and their 2,2′-bypyridine and 1,10-phenanthroline adducts, while comparatively little is known on VO(IV), Co(II), Ni(II), and Cu(II) complexes of unsymmetrical Schiff bases derived from condensation of 2-hydroxy-4-methoxyacetophenone or 2-hydroxy-4-methoxybenzophenone and 2,4-pentanedione or 1-phenyl-1,3-butanedione with ethylenediamine and the adducts formed with triphenyphosphine. Structural diversities arising from changes in combinations of aromatic hydroxyl aldehydes/β-diketones and changes in substituents in these carbonyl compounds in the Schiff bases have been reported. We also reported some antimicrobial activities which were sensitive to the metal complexes as well as the adducts.

In continuation of our work on unsymmetrical Schiff-base chelates and their adducts, we report here the synthesis and characterization of two isomeric unsymmetrical Schiff bases involving the condensation of 2-hydroxy-4-methoxyacetophenone/2-hydroxy-4-methoxybenzophenone with 2,4-pentanedione/1-phenyl-1,3-butanedione and ethylenediamine, their VO(IV), Ni(II), Co(II), and Cu(II) complexes, and the complexes formed when each of these complexes reacts with triphenylphosphine. It was expected that the two isomeric ligands reported in this work would have structural diversity when coordinated to different metal(II) ions due to the location of the functional groups on the carbonyl compounds that are condensed to form each ligand. The two ligands and the metal complexes reported in this work are new, but similar to those that recently emerged from our laboratories [29]. We also report the spectral and magnetic properties of the complexes.

2. Experimental

2.1. *Reagents and solvents*

Reagent grade 2,4-pentanedione, 1-phenyl-1,3-butanedione, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-acetophenone, ethylenediamine, and triphenylphosphine were obtained from Aldrich, while oxovanadium(IV) sulfate-1-water, cobalt(II) acetate-4-water, nickel(II) acetate-4-water, and copper(II) acetate-1-water were obtained from BDH chemicals. All chemicals were used as received.

2.2. *Preparation of the Schiff bases*

$[HO(C_6H_3(OCH_3)C(C_6H_5):N(CH_2)_2N:C(CH_3)CH:C(CH_3)OH)]$, H_2L^1 (**1**) was prepared by a method we previously reported [27] by stirring 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 (10.01 g, 10.46 mL) of 2,4-pentanedione in 100 mL of ethanol. Corresponding quantity for 2-hydroxy-4-methoxy-acetophenone and 1-phenyl-1,3-butanedione was 16.22 g each in the preparation of $[HO(OCH_3)C_6H_3C(CH_3):N(CH_2)_2N:C(CH_3)CH:C(C_6H_5)OH]$, H_2L^2 (**2**). Each reaction mixture was refluxed for 2 h and the products were filtered and washed with ethanol and dried over anhydrous calcium chloride. Yields were 25.4 g (80%) for H_2L^1 (**1**) and 24.7 g (70%) for H_2L^2 (**2**); m.p. (**1**) 198–199°C; (**2**) 142–143°C; analyses (%): $C_{21}H_{24}N_2O_3$, Found (Calcd) (**1**): C, 71.20 (71.57); H, 6.74 (6.86); N, 8.53 (7.95); (**2**): C, 72.00 (71.57); H, 6.66 (6.86); N, 7.89 (7.95).

2.3. *Preparation of the metal(II) complexes*

[ML], M = Ni(II), Co(II), Cu(II) and VO(IV); L = $L^{1\ 2-}$ and $L^{2\ 2-}$ were prepared by addition of 5 mmol of $Ni(CH_3COO)_2 \cdot 4H_2O$ (1.24 g), $Co(CH_3COO)_2 \cdot 4H_2O$ (1.26 g), $Cu(CH_3COO)_2 \cdot H_2O$ (1.00 g), or $VOSO_4 \cdot H_2O$ (0.82 g), dissolved in 40% aqueous ethanol (30 mL), to stirring 5 mmol of each ligand (1.76 g) in hot absolute ethanol (50 mL). The oxovanadium(IV) reaction mixture was buffered with 10 mmol (1.02 g) of triethylamine. The color of the complexes changed in few minutes. Each mixture was refluxed for 2 h and the products formed as solids on cooling, were filtered, washed with ethanol, and dried over anhydrous calcium chloride. The cobalt complexes of **2** gave poor analysis and are therefore excluded from this work.

2.4. *Preparation of the adducts [ML(PPh$_3$)(H$_2$O)]*

To a suspension of 5 mmol of each of the complexes in 20 mL of ethanol on a hotplate stirrer was added slowly to a solution of 2.62 g (10 mmol) of triphenylphosphine dissolved in 10 mL of ethanol. The mixture was refluxed for 2 h and the product formed was cooled, filtered, washed with ethanol, and dried over anhydrous calcium chloride. Triphenylphosphine coordinated with all the complexes to form adducts $[ML^1(PPh_3)_2]$ and $[ML^2(PPh_3)(H_2O)]$ in pure form except VOL^1, which could not be isolated.

2.5. *Physical measurements*

Microanalyses for C, H, N were performed by the South African Bureau of Standards and the Dipartmento discienze Chimiche, Universita di Trieste, Italy. Vanadium was analyzed gravimetrically by converting a known mass of complex to V_2O_5 in a furnace at 500°C, while cobalt, nickel, and copper were determined by complexometric titration. The solution electronic spectra in chloroform were recorded on a Unicam Helios γ-spectrophotometer. The infrared spectra of the compounds were measured as KBr discs on a Perkin–Elmer FTIR Paragon 1000 spectrophotometer in the range 4000–400 cm^{-1}. Magnetic susceptibilities were measured at room temperature (23 ± 1°C) on a Johnson Matthey magnetic susceptibility balance using $Hg[Co(NCS)_4]$ as reference. Diamagnetic corrections were calculated using Pascal's constants.

Electrolytic conductivity on 10^{-3} M solution in DMF of each compound was determined using a MC–1, Mark V conductivity meter with a cell constant of 1.0. Each solution was allowed to equilibrate at room temperature ($23 \pm 1°C$) for 30 min before taking a measurement.

3. Results and discussion

The formation of two isomeric Schiff bases (**1** and **2**) is confirmed by microanalyses, which eliminates formation of the symmetrical Schiff bases from either the 2 : 1 condensation of the aldehyde or the β-diketone with ethylenediamine. The melting points of 198–199°C and 142–143°C for **1** and **2** and the yellow and light yellow colors, respectively, eliminate *bis*-(acetylacetonato)ethylenediimine (straw-colored) and *bis*(1-phenyl-1,3-butanedionato)ethylenediimine (white) [30], which melt at 111–111.5°C and 180.5°C, respectively. Formation of the symmetrical Schiff base derived from aromatic carbonyls and ethylenediamine can be easily distinguished from the microanalyses.

A reaction scheme is provided for formation of the complexes and adducts in figure 1. Complexes of **1** formed at relatively lower yields (20–50%) than those formed from **2** (40–70%). At molar conductivity lower than 15 $\mathrm{Ohm^{-1}\,cm^2\,mol^{-1}}$, the complexes are nonelectrolytes in DMF, although partial decomposition could not be ruled out. The analytical data, colors, percentage yields, melting points/decomposition temperatures, molar conductivities, and room temperature magnetic moments of the complexes are presented in table 1.

3.1. *Electronic spectra*

A square-pyramidal geometry is usually assumed for oxovanadium(IV) complexes. Theoretical models developed around this regular geometry are found to be only partially satisfactory for interpreting magnetic and spectral properties of some oxovanadium(IV) complexes, especially low-symmetry complexes. Patel *et al.* [31] provided experimental evidence for the diversity of symmetry for low-symmetry, Schiff-base complexes, and proposed an energy level scheme that accommodates such diversity within Ballhausen and Gray energy level sequences [32]. To interpret the electronic spectra of the oxovanadium(IV) complexes reported in this work (table 2, figure 2), the sequence: $b_2\ (d_{xy}) < e_\pi^*\ (d_{xz}, d_{yz}) < b_1^*\ (d_{x^2-y^2}) < a_1^*\ (d_{z^2})$ is adopted. Patel *et al.* [31] and Kolawole and Patel [33], however, provided some evidence for inversion of the e_π^* and b_1^* energy levels in a series of VO(IV) complexes of low-symmetry Schiff bases involving long chain alkyl-bridged diamines.

Electronic spectra in chloroform of both oxovanadium(IV) complexes gave three absorption bands at 14.88, 17.81, and 23.26 kK (for [VOL^1]), and 15.80, 18.35, and 23.87 kK (for [VOL^2]), typical of 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). The higher intensities of the bands in [VOL^2] could be due to the presence of CH_3 next to the azomethine, providing less resonance hybridization than the second benzene ring provides in [VOL^1]. Resonance stabilization, therefore, appears more important than

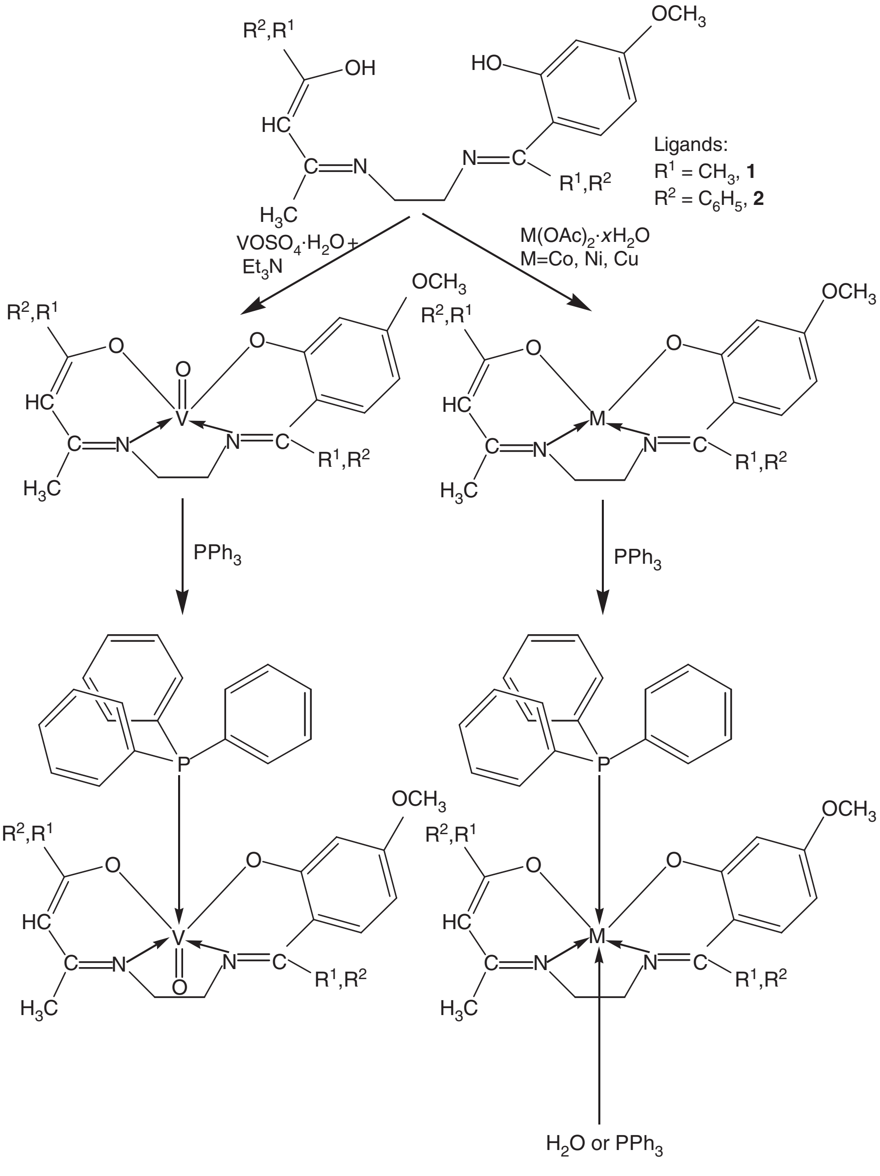

Figure 1. Reaction scheme for the formation of the complexes and adducts.

steric destabilization in these complexes, implying that the V is closer to the basal plane of the donor atoms in [VOL^1] than in [VOL^2], and therefore is more planar. This is further confirmed from the V=O stretching frequency of [VOL^1], which is lower (940 cm^{-1}) than for [VOL^2] (968 cm^{-1}) (table 3). However, steric effects prevent formation of the adduct in [VOL^1], despite its more planar structure. Incorporation of PPh_3 into [VOL^2] is evident in the electronic spectrum of the adduct, which changes to distorted octahedral (figure 1). Retention of the band at about 18.87 kK, but at lower molar, is an indication that the perturbation of square-pyramidal geometry is weak and the V–P(Ph$_3$)$_3$ bond length could be long.

Table 1. Analytical data for the complexes.

Compound					Analysis: Found (Calculated)					
(Empirical formula)	Formula mass	Color	Yield (%)	m.p. (°C)	% C	% H	% N	% Metal	μ_{eff} (B.M.)	Λ_m[a]
$[VOL^1]$	417.36	Green	30	130–132	59.89	5.40	7.00	12.00	1.76	10.80
$[VOL^2]$		Green	70	210–211	60.49	5.29	6.72	12.25	1.74	11.67
$VOC_{21}H_{22}O_3N_2$					(60.43)	(5.31)	(6.71)	(12.21)		
$[VOL^2(PPh_3)]$	680.28	Green	40	202–203	68.96	5.45	4.10	7.51	1.75	10.42
$(VC_{39}H_{37}N_2O_4P)$					(68.68)	(5.48)	(4.12)	(7.49)		
$[CoL^1]$	409.35	Greenish yellow	20	260–261	61.60	5.60	6.74	13.53	4.40	10.62
$(CoC_{21}H_{22}N_2O_3)$					(61.62)	(5.42)	(6.84)	(14.4)		
$[CoL^1(PPh_3)_2]$	933.93	Green	30	147	72.89	6.00	3.10	6.00	5.20	9.83
$(CoC_{57}H_{52}O_3N_2P_2)$					(73.31)	(5.61)	(3.00)	(6.31)		
$[NiL^1]$	409.13	Orange	30	200–202	61.72	5.30	7.00	14.00	0	11.20
$[NiL^2]$		Yellow	70	256–258	61.62	5.41	7.00	14.60	0	10.66
$(NiC_{21}H_{22}O_3N_2)$					(61.65)	(5.42)	(6.85)	(14.40)		
$[NiL^1(PPh_3)(H_2O)]$	689.44	Yellowish orange	30	234–235	67.60	6.10	4.10	8.30	3.10	10.45
$[NiL^2(PPh_3)(H_2O)]$		Orange	40	220–221	67.81	5.51	4.10	8.29	3.03	11.00
$(NiC_{39}H_{39}O_4N_2P)$					(67.94)	(5.70)	(4.06)	(8.52)		
$[CuL^1]$	413.97	Purple	30	260–262	61.00	5.50	6.68	14.90	1.90	11.02
$[CuL^2]$		Purple	70	240–242	60.75	5.40	6.78	16.00	1.92	11.57
$(CuC_{21}H_{22}O_3N_2)$					(60.93)	(5.36)	(6.76)	(15.35)		
$[CuL^1(PPh_3)_2]$	694.28	Purple	50	> 230	72.51	5.61	3.01	6.00	2.15	9.85
$(CuH_{57}H_{52}O_3N_2P_2)$		Brown	40	220–222	(72.95)	(5.59)	(2.99)	(6.77)		
$[CuL^2(PPh_3)(H_2O)]$					69.31	5.47	4.00	9.17	2.04	10.21
$(CuC_{39}H_{39}N_2O_4P)$					(67.47)	(5.66)	(4.04)	(9.15)		

Note: [a]$\Omega^{-1}\,cm^2\,mol^{-1}$.

Table 2. Electronic spectral data for the complexes.

Compounds	*d–d* band positions/kK, $1\,\text{kK} = 1000\,\text{cm}^{-1}$ ($\varepsilon\,\text{cm}^2\,\text{mol}^{-1}$)
[VOL^1]	14.88 (70), 17.81(100), 23.26 (200)
[VOL^2]	15.80 (100), 18.35 (145), 23.00 (300)
[VOL^2(PPh$_3$)]	12.90 (180) 18.87 (150), 25.00 (300)[a]
[CoL^1]	12.00 (10), 17.00 (150), 25.0 (200)
[CoL^1(PPh$_3$)$_2$]	12.35 (75), 13.74 (90), 17.24 (100)
[NiL^1]	18.32 (200), 23.40 (500)
[NiL^2]	18.00 (100), 24.00 (1000)
[NiL^1(PPh$_3$)(H$_2$O)]	18.18 (70), 23.0 (150), 25.0 (200)
[NiL^2(PPh$_3$)(H$_2$O)]	17.60 (180), 23.40 (800), 24.04 (1000)
[CuL^1]	18.05 (200), 23.98 (300)
[CuL^2]	18.12 (400), 24.94 (1000)
[CuL^1(PPh$_3$)$_2$]	13.89 (40), 17.86 (50)
[CuL^2(PPh$_3$)(H$_2$O)]	18.18 (200)

Note: [a]Not shown on the spectrum in figure 3.

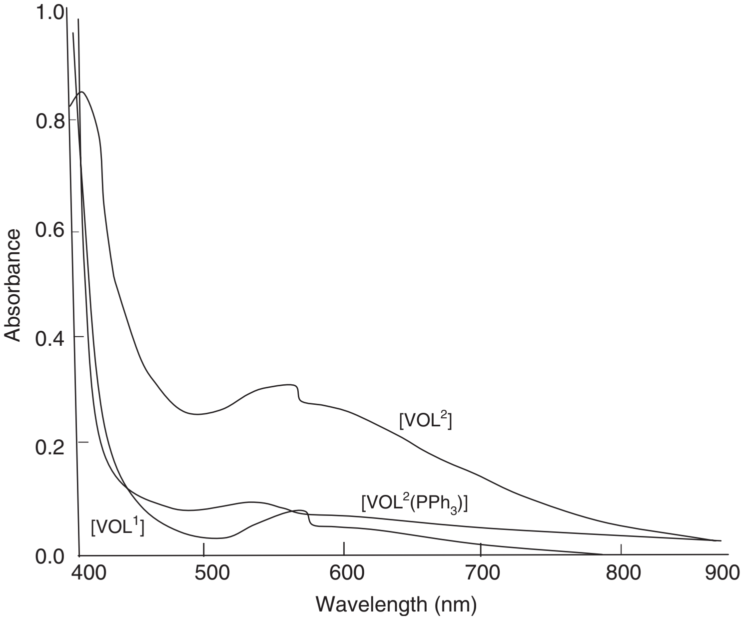

Figure 2. Electronic spectra of the oxovanadium(IV) complexes.

The cobalt(II) complex of **1** gave three absorption bands at 12.00, 17.00, and 25.00 kK, while its adduct has two bands at 13.74 and 17.24 kK. The absorption spectral pattern of the former indicates four-coordinate tetrahedral geometry, and the bands are therefore assigned to $^4A_2 \rightarrow {}^4T_1(\text{F})$ (ν_2) and $^4A_2 \rightarrow {}^4T_1(\text{P})$ (ν_3). The assignment of a tetrahedral geometry is supported by the micro-analytical and the magnetic data. However, the location of transition $^4A_2 \rightarrow {}^4T_2$ (ν_1) in the range 5–7 kK is outside the range covered by the instrument. The absorption pattern of the adduct, on the contrary, is consistent with a six-coordinate octahedral geometry and assigned to $^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$ (ν_2) and $^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ (ν_3) transitions. The transition

Table 3. Relevant infrared spectral data of the compounds.

Compound	νOH	νV=O	νC=N	νC=C	νM–N	νM–P	νM–O
H_2L^1	3200 s		1595 s	1508 s			
H_2L^2	3375 s		1596 s	1543 s			
$[VOL^1]$		940 vs	1592 s	1515 s	595 s		434 s
$[VOL^2]$		965 vs	1589 s	1513 s	595 s		470 m
$[VOL^2(PPh_3)]$		925 vs	1606 s	1545 s	590 s	520 s	426 m
$[CoL^1]$			1593 s	1566 s 1535 s	581 s		497 s
$[CoL^1(PPh_3)_2]$			1588 s	1460 s	553 s	540 m	495 s
$[NiL^1]$			1570 s	1527 s	594 s		435 s
$[NiL^2]$			1571 s	1531 s	595 s 560 s		450 m
$[NiL^1(PPh_3)(H_2O)]$	3500 b		1521 s	1460 s	550 s	538 m	425 s
$[NiL^2(PPh_3)(H_2O)]$	3500 b		1592 s	1574 s	559 s	542 s	496 m
$[CuL^1]$			1588 s	1527 s	568 s		468 s
$[CuL^2]$			1593 s	1519 s	519 s 535 s		465 m
$[CuL^1(PPh_3)_2]$			1562 s	1507 s	594 s	558 m	467 s 415 s
$[CuL^2(PPh_3)(H_2O)]$	3500 b		1600 m	1548 s	589 s	523 s	450 m

Note: b = Broad; s = Strong; m = Medium; vs = Very strong.

expected in the range 11–12 kK, $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ν_1, was not observed since it is expected to be weak [35]. Normally, the molar extinction coefficient (ε) allows a distinction of tetrahedral geometry from octahedral geometry. Tetrahedral complexes are expected to have a higher molar extinction coefficient in the range 10^2–$10^3\,cm^2\,mol^{-1}$ and octahedral complexes should have ε between 1–50 $cm^2\,mol^{-1}$. The cobalt(II) complex has ε of 100–300 $cm^2\,mol^{-1}$ suggestive of a tetrahedral geometry while its adduct has a molar extinction coefficient in the range 90–100 $cm^2\,mol^{-1}$, considered relatively high for an octahedral complex and appears to have been enhanced by the π system of the ligand and the axial base [34].

Nickel(II) complexes can undergo structural switches from four-coordinate square planar to tetrahedral or to six-coordinate octahedral [35, 36]. The observance of two bands in the absorption spectrum of $[NiL^1]$ in chloroform at 18.32 and 23.40 kK is consistent with square-planar geometry and assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow A_{2g}$, respectively [37]. Its adduct has three absorption bands at 18.12, 23.00, and 25.00 kK, assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions of a six-coordinate nickel complex [38]. Corresponding transitions in $[NiL^2]$ and $[NiL^2((PPh_3)_3)(H_2O)]$ occur at 18.00 and 24.00 kK, and 17.60, 23.40, and 24.04 kK, respectively. The assignment of absorption bands of the nickel complexes is corroborated by the diamagnetism of $[NiL^x]$ and the paramagnetism of the adducts.

In a cubic environment copper(II) is susceptible to Jahn Teller distortions, giving rise to unsymmetrical or multiple bands. A maximum of three transitions are predicted in the visible spectra of octahedral complexes of copper(II). Tetrahedral copper(II) complexes are not very common. However, clear distinction can be made between square planar and tetrahedral geometries. In a regular tetrahedral environment, a single broad band of $\sim 10^2$ molar intensity in the near infrared region is observed with the spectra being blank between 10.0 and 20.0 kK [34]. Structural similarities are evident in the two precursor copper(II) complexes reported in this work, which displayed bands at 18.05 and 23.98 kK $[CuL^1]$ and 18.12 and 25.00 kK $[CuL^2]$ assigned to *d–d* transitions

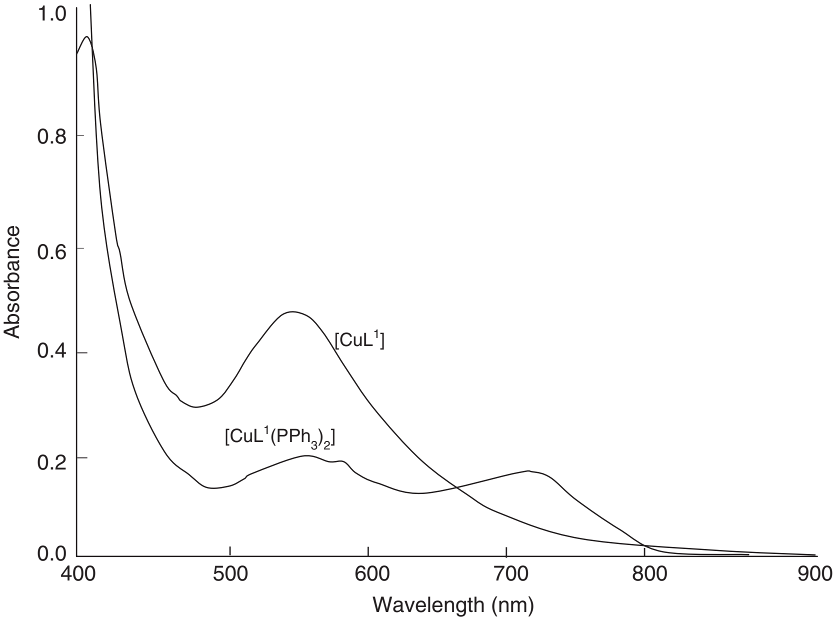

Figure 3. Electronic spectra of the copper complexes of **1** and the adduct.

of a tetrahedral/distorted square-planar geometry, assuming a tetrahedral geometry in solution lies in the relatively high molar absorbance of the two *d–d* transitions in each case (200–300 cm^2 mol^{-1} for [CuL^1] and 400–1000 cm^2 mol^{-1} for [CuL^2]). However, [CuL^1(PPh$_3$)$_2$] displays two bands at 13.89 and 17.86 kK with molar absorbance of 40 and 50 cm^2 mol^{-1}, whereas [CuL^2(PPh$_3$)(H$_2$O)] displays an unsymmetrical band at 18.18 kK ($\varepsilon = 200$ cm^2 mol^{-1}), indicating a six-coordinate distorted octahedral arrangement around the copper [34]. The distortion of [CuL^1(PPh$_3$)$_2$] reflects in the shoulders that flanked the band at 17.86 kK (figure 3). One unsymmetrical band in [CuL^2(PPh$_3$)(H$_2$O)] is an indication of **2** exerting a larger ligand field that makes crystal field splitting larger in [CuL^2(PPh$_3$)(H$_2$O)]. The relatively high molar absorbance (200–1000 cm^2 mol^{-1}) observed in the octahedral adducts reported in this work could be attributed to an intimate interaction of metal orbitals with the ligands' delocalized π-system.

3.2. *Infrared spectra*

Relevant infrared bands of the compounds are presented in table 3. The O–H stretching frequency expected at 3300–3800 cm^{-1} was observed at 3200 cm^{-1} in **1** and at 3375 cm^{-1} in **2**. The displacements are due to intramolecular hydrogen-bonding, usually very strong in Schiff bases [38]. This band disappeared in spectra of the complexes due to the replacement of the hydrogen by metal on complex formation. Coordination of the enol O to the metal ions is thus confirmed. The broad band at 3500 cm^{-1} in the spectra of [NiL^1(PPh$_3$)(H$_2$O)] and [NiL^2(PPh$_3$)(H$_2$O)] is assigned to νOH of the coordinated H$_2$O.

C=N stretching frequencies occur at about the same position, 1595 cm^{-1} (in **1**) and 1596 cm^{-1} (in **2**), and νC=C at 1508 and 1543 cm^{-1}, respectively. Both bands are coupled as expected [27, 28]. [VOL^1] gave only one band at $1515\,cm^{-1}$ in this region, indicating a substantial shift due to stronger involvement of the VO π-system in the extended conjugation of the ligand benzene rings and the azomethine group. On the other hand, $\nu C{=}N$ and $\nu C{=}C$ for [VOL^2] were observed at 1589 and $1513\,cm^{-1}$, respectively, reflecting weaker involvement of the VO π-system in conjugation because of the absence of a second aromatic ring. Corresponding bands for other complexes of **1** occur at 1588–1598 cm^{-1} ($\nu C{=}N$) and 1527–1535 cm^{-1} ($\nu C{=}C$) and for complexes of **2** at 1571–1593 and 1519–1531 cm^{-1}, respectively. These shifts indicate involvement of the azomethine N in coordination to metal(II). Upon adduct formation further bathochromic shifts of this coupled band were observed at 1588 and $1460\,cm^{-1}$ (for [$CoL^1(PPh_3)_2$]), 1521 and $1527\,cm^{-1}$ (for [$NiL^1(PPh_3)(H_2O)$]) and 1562 and $1507\,cm^{-1}$ (for [$CuL^1(PPh_3)_2$]). Similar trends were observed for adducts of complexes of **2**. This shift is, therefore, an indication of the formation of a M–P bond in the adducts [27, 28].

Formation of M–P bond is further corroborated by the appearance of an additional band in the adducts in the range 400–600 cm^{-1} due to νM–P [39], absent in the precursor complexes. The bands due to νM–O, νM–N, and νM–P are consequently assigned at 497–415, 595–550, and 594–550 cm^{-1}, respectively, for complexes of **1** and at 496–426, 595–559, and 542–520 cm^{-1}, respectively, for complexes of **2**.

The stretching frequencies due to V=O occur, as very strong bands, at $940\,cm^{-1}$ (for [VOL^1]) and $968\,cm^{-1}$ (for [VOL^2], within the lower end of the range expected of a VO^{2+} complex in a square-pyramidal environment, indicating that the V=O bond might have been subjected to some perturbation at the axial position [31]. In [VOL^1] the vanadium is much closer to the plane of the donor atoms than in [VOL^2]. Normally in distorted octahedral complexes, found with V–O–V linkages, $\nu V{=}O$ is at $860 \pm 20\,cm^{-1}$ [31, 32]. A frequency of $925\,cm^{-1}$ in [$VOL^2(PPh_3)$], a shift of $40\,cm^{-1}$ to lower frequency than [VOL^2], indicates that the triphenylphosphine is coordinated. However, the location of the band is much higher than usually observed for distorted octahedral complexes involving V–O–V linkages; consequently, the V–P bond is expected to be much longer than in V–O in V–O–V.

3.3. *Magnetic moments*

In the absence of metal–metal interaction, oxovanadium(IV) complexes are expected to have a moment in the vicinity of 1.73 B.M., regardless of the geometry. A moment of 1.76 B.M. was observed for [VOL^1], 1.74 B.M. for [VOL^2] and 1.75 B.M. for [$VOL^2(PPh_3)$], all normal for monomeric d^1 complexes.

All tetrahedral cobalt(II) d^7 complexes are expected to have spin-only magnetic moments. However, our observation for [CoL^1], along with data [40] for a number of other tetrahedral Co(II) complexes, shows that tetrahedral Co(II) complexes do possess orbital contributions to their magnetic moments. According to Holm and Cotton [41] this orbital contribution may be in the range of 0.2–1.1 B.M., depending on the nature of the ligands. A moment of 4.40 B.M. observed for [CoL^1] falls within this range, in agreement with absorption spectral data. Octahedral Co(II) complexes are expected to have moments between 4.70–5.20 B.M., consistent with the adduct of 5.20 B.M.

The structural switches of Ni(II) complexes can easily be established by magnetic susceptibility measurements. Generally, square-planar complexes are diamagnetic, while tetrahedral complexes have moments in the range 3.20–4.10 B.M. and octahedral complexes should have moments between 2.90 and 3.30 B.M. The Ni(II) complexes for both ligands are diamagnetic, confirming square-planar geometries while the adducts have moments of 3.10 B.M. (for **1**) and 3.03 B.M. (for **2**) typical of octahedral complexes [40].

The room temperature magnetic moments of copper(II) complexes are expected to be higher than the spin-only value of 1.73 B.M. as a result of spin-orbit coupling. Consequently, moments of 1.9–2.2 B.M. are normal for mononuclear copper(II) complexes, regardless of stereochemistry [40]. The effective magnetic moments of the copper complexes and the adducts for both ligands were between 1.90 and 2.15 B.M., indicating they are all magnetically dilute.

4. Conclusion

The unsymmetrical Schiff bases coordinate to VO(IV), Co(II), Ni(II), and Cu(II) using the azomethine N and the enol O atoms to form four-coordinate complexes. The involvement of the enol O and axomethine N in coordination is confirmed by infrared spectroscopy. The shift in the $\nu V{=}O$ of $[VOL^2(PPh_3)]$ helps in establishing the coordination of PPh_3 to $[VOL^2]$, and, by extension, to the Ni(II) and Co(II) Schiff-base complexes, which are expected to be more planar. The assignment of a square-planar geometry to the Ni(II) complexes is confirmed by their diamagnetism, while the geometries of the Co(II) and Cu(II) complexes and the adducts are confirmed by microanalyses, magnetic, and spectroscopic data. In the absence of suitable crystals for single crystal structural studies, possible structural formula for the complexes and the adducts are shown in figure 1.

Acknowledgments

The authors thank South African Bureau of Standards and Dipartmento di Scienze Chimiche, Universita di Trieste, Italy. GAK also acknowledges financial support from National Research Foundation (South Africa) and the Royal Society (UK).

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