

Some Copper(II) Complexes of Tetradentate β -Ketoimines and their Adducts

Aderoju A. Osowole

Department of Chemistry, University of Ibadan, Ibadan, Nigeria

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Abstract. The β -ketoimine ligands $\{[\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{CH}_3)(-\text{NH}(\text{CH}_2)_n\text{NH}-)\text{C}(\text{CH}_3)\text{CHC}(\text{O})\text{CH}_3]; n = 2, 6, 8, 9\}$, their copper(II) chelates, and adducts with 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) have been synthesized and characterized by elemental analysis, magnetic susceptibility, conductance, and infrared and electronic spectral measurements. The ligands were tetradentate in the complexes, using the imine N and keto O atoms in coordination. The room temperature magnetic moments of the complexes, suggest that they were magnetically dilute, while infrared and electronic spectra results were corroborative of a four coordinate square-planar geometry for the copper(II) chelates and a six coordinate octahedral geometry for their adducts. The compounds were non-electrolyte in nitromethane.

Keywords: 2,2'-bipyridine adducts, β -ketoimines, square-planar geometry, tetradentate ligands, octahedral geometry, copper(II) chelates

Introduction

Ketoamines, ketoiminies/Schiff bases, and their metal(II) chelates, have been studied due to their high reactivity in catalysis (Britovsek *et al.*, 2001; Gade, 2001; Laine *et al.*, 1999). For example, zirconium ketoiminates and their derivatives have been reported to have moderate activity for the polymerization of ethylene in the presence of cocatalyst-modified methylaluminumoxane (Kim *et al.*, 2001; Britovsek *et al.*, 1999), while vanadyl tetradentate Schiff base complexes were used as catalysts in aerobic selective oxidation of olefins and cyclohexene (Boghaei and Mohebi, 2002). The ternary Cu(II) chelates of amino acid Schiff bases have found uses in intermolecular crossings, or as immobilizing agents for proteins and as oxidative cleaving agents for DNA in the presence of mercaptopropionic acid (Reddy and Kandibanda, 2006; Katsuhiko *et al.*, 1989).

Polymeric Schiff bases derived from 2,7-diaminofluorene, terephthalaldehyde or glyoxal are used as semi-conductors in appliances (Danhaeuser and Manecke, 1965), while Schiff bases derived from hexamethylenediamine and anisaldehyde or *p*-(dimethylamino)benzaldehyde increased the tensile strength of rubber formed when cross-linked with hexafluoropropylene and vinylidene fluoride, or are used to improve ageing resistance of natural rubber (George *et al.*, 1993; Dobrokhotov and Makarov, 1978). Schiff bases are used as corrosion inhibitors. For example, fluorinated Schiff base derived from 3,4-difluorobenzaldehyde and 4,4'-benzidine has been used as corrosion inhibitor in steel (Mehta and Agarwala, 1996). Furthermore, these ligands are planar, highly

E-mail: aderoju30@yahoo.com

acidic with unique chelating ability, and may serve as models for biological studies (Sorell, 1989). In medicine, the Schiff base derived from S-benzylthiocarbamate and benzil, and its Cd(II) and Zn(II) complexes, have high activity against renal and melanoma carcinoma (Tofazzal *et al.*, 2000).

A search through literature reveals detailed information on copper(II) complexes of various salicyaldimines, naphthaldimines, 3-chloro- β -ketoimines and fluorinated analogs with their pyridine(s), 2,2'-bipyridine or 1,10-phenanthroline adducts (Osowole *et al.*, 2003, Abd-Elzaher, 2001; Kabak *et al.*, 1999; Mehta and Desai, 1998; Abuhijleh and Ahmed, 1991), whereas very little is known about Cu(II) β -ketoiminates derived from condensation of 2,4-pentanedione and aliphatic diamines and their 2,2'-bipyridine and 1,10-phenanthroline adducts. Attempt was, therefore, made to synthesise and characterize various β -ketoimines, their copper(II) complexes and adducts with 2,2'-bipyridine (bipy), and 1,10-phenanthroline (phen). The effect of increasing methylene chain from 2-9 in the copper(II) complexes on their geometry was also investigated. The ligands used for the study and their acronyms (H_2L^1 , H_2L^2 , H_2L^3 and H_2L^4) are shown in Fig. 1 (equations 1-3). These ligands (Woods *et al.*, 2004; Osowole *et al.*, 2002), and $[\text{Cu}(\text{L}^3)]$ (Holtzclaw *et al.*, 1958; McCarthy *et al.*, 1955) have been reported in literature. However, other Cu(II) compounds and all the adducts are new, which are being reported here for the first time.

Materials and Methods

Analytical procedures. The elemental analyses for C, H and N were done at the Microanalytical Laboratory, Institute of

Organic Chemistry, TuDarmstadt, Germany. Copper was determined titrimetrically (Bassett and Vogel, 1978). The diffuse reflectance spectra were recorded on a Perkin-Elmer λ 20 spectrophotometer, while the infrared spectra of complexes were measured as KBr discs on a Perkin-Elmer SP 500 spectrophotometer; frequencies were accurate within $\pm 2 \text{ cm}^{-1}$. Magnetic susceptibilities were measured on Johnson Matthey magnetic susceptibility balance and diamagnetic corrections were calculated using Pascal's constant (Earnshaw, 1968). Electrolytic conductivities of the soluble compounds in nitromethane were determined using a MC-1, Mark V conductivity meter with a cell constant of 1.0.

Preparation of the ligands. For the preparation of $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{CH}_3)(-\text{N}(\text{CH}_2)_n\text{N}-)\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{CH}_3]$ (H_2L^2), a solution of 2,4-pentanedione (4.00 g, 40 mmol) and hexamethylenediamine (2.32 g, 20 mmol) in 100 ml of benzene and two drops of conc HCl was refluxed in a flask equipped with a Dean-Stark trap for 4 h. The solvent was removed under vacuum to obtain the ligand compound; yield, 4.49 g (80%). The same procedure was used to prepare $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{CH}_3)(-\text{N}(\text{CH}_2)_n\text{N}-)\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{CH}_3]$ for: $n = 2$ (H_2L^1); $n = 8$ (H_2L^3); and $n = 9$ (H_2L^4). The scheme for the synthesis of ligands is given in Fig. 1(1).

Synthesis of copper(II) complexes. For the preparation of $\text{Cu}[\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{CH}_3)(-\text{N}(\text{CH}_2)_6\text{N}-)\text{C}(\text{CH}_3)\text{CHC}(\text{O})\text{CH}_3]$, (CuL^2), $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$ (3.99 g, 20 mmol) in 40 ml of 50% ethanol was added dropwise to the ketoimine, $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{CH}_3)(-\text{N}(\text{CH}_2)_6\text{N}-)\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{CH}_3]$ (5.61 g, 20 mmol) in 50 ml ethanol while stirring, followed by the addition of dimethoxy propane (2.07 g, 20 mmol). The mixture was stirred for 1 h at 40°C , after which the resulting precipitate was filtered and washed with ethanol and dried in vacuum over CaCl_2 . A similar procedure was used to prepare the other copper(II) complexes. The scheme for the synthesis of copper(II) complexes is given in Fig. 1(2).

Synthesis of the adducts. For the preparation of $[\text{Cu}\{\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{CH}_3)(-\text{N}(\text{CH}_2)_6\text{N}-)\text{C}(\text{CH}_3)\text{CHC}(\text{O})\text{CH}_3\}(\text{bipy})]$, $[(\text{CuL}^2)(\text{bipy})]$, 2,2'-bipyridine (1.72 g, 10 mmol) dissolved in 10 ml of chloroform was added to a solution of $\text{Cu}[\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{CH}_3)(-\text{N}(\text{CH}_2)_6\text{N}-)\text{C}(\text{CH}_3)\text{CHC}(\text{O})\text{CH}_3]$ (3.42 g, 10 mmol) dissolved in 20 ml of chloroform while stirring. The mixture was refluxed at 70°C for 1 h. The precipitate was filtered and washed with the minimum amount of chloroform, and dried in vacuum over CaCl_2 . Similar procedure was used to prepare the other 2,2'-bipyridine and 1,10-phenanthroline adducts of the copper(II) complexes. The scheme for the synthesis of adducts is given in Fig. 1(3).

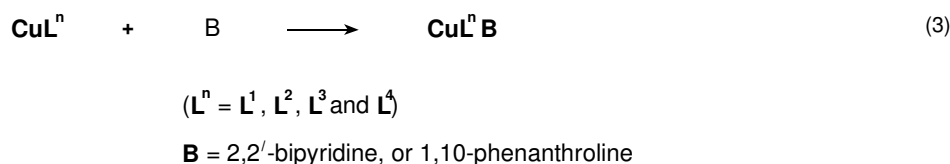
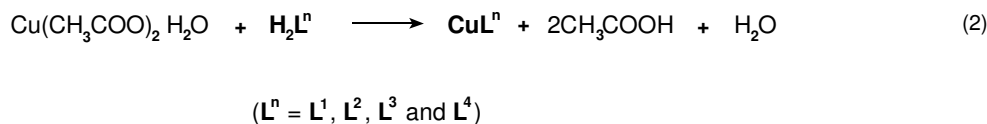
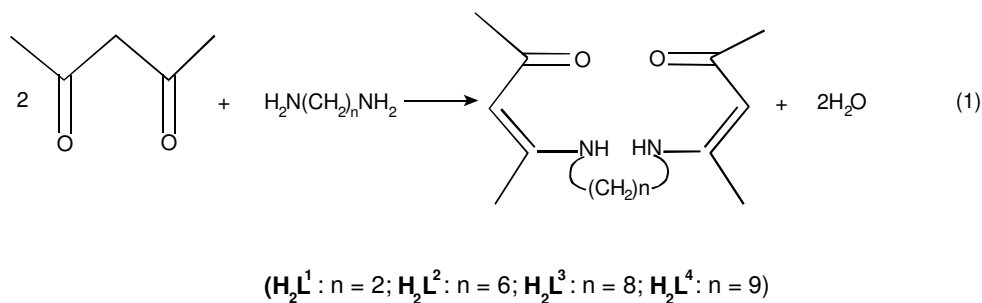


Fig. 1. Scheme for the synthesis of: (1) ligands; (2) copper complexes; (3) adducts.

Table 1. Analytical data for the ligands and complexes

Compounds (empirical formula)	Formula weight	Colour	Yield (%)	m.p. (°C)	C, H, N analysis found (calculated)*			Cu (%)	Magnetic moment (μ_{eff})
					C	H	N		
H₂L¹ (C ₁₂ H ₂₀ N ₂ O ₂)	224.31	yellow	60	111-113	64.45 (64.26)	8.66 (8.99)	12.45 (12.49)	-	-
[Cu(L¹)] (C ₁₂ H ₁₈ N ₂ O ₂ Cu)	286.85	dark purple	30	149-150	50.21 (50.25)	6.40 (6.33)	9.82 (9.77)	22.16 (22.15)	1.66
[Cu(L¹)(bipy)] (C ₂₂ H ₂₆ N ₄ O ₂ Cu)	443.03	red	60	129-130	59.73 (59.74)	5.92 (5.92)	12.68 (12.65)	14.00 (14.34)	1.57
H₂L² (C ₁₆ H ₂₈ N ₂ O ₂)	280.41	yellow	80	76-78	68.25 (68.53)	10.21 (10.07)	9.75 (9.99)	-	-
[Cu(L²)] (C ₁₆ H ₂₆ N ₂ O ₂ Cu)	341.94	dark blue	50	153	56.00 (56.20)	7.69 (7.67)	8.20 (8.19)	18.60 (18.59)	1.98
[Cu(L²)(bipy)] (C ₂₆ H ₃₄ N ₄ O ₂ Cu)	498.13	green	50	220	62.68 (62.69)	6.87 (6.89)	11.25 (11.25)	12.70 (12.76)	2.20
[Cu(L²)(phen)] (C ₂₈ H ₃₄ N ₄ O ₂ Cu)	522.15	blue	40	206	64.42 (64.41)	6.56 (6.56)	10.73 (10.73)	12.00 (12.17)	2.20
H₂L³ (C ₁₈ H ₃₂ N ₂ O ₂)	308.46	brown	70	98-100	70.24 (70.09)	10.66 (10.46)	8.95 (9.08)	-	-
[Cu(L³)] (C ₁₈ H ₃₀ N ₂ O ₂ Cu)	370.00	dark blue	50	123	58.40 (58.43)	8.15 (8.17)	7.56 (7.57)	17.20 (17.18)	2.01
[Cu(L³)(bipy)] (C ₂₈ H ₃₈ N ₄ O ₂ Cu)	526.19	blue	50	170	63.70 (63.91)	7.27 (7.28)	10.67 (10.65)	12.10 (12.08)	2.17
[Cu(L³)(phen)] (C ₃₀ H ₃₈ N ₄ O ₂ Cu)	550.21	blue	50	220	65.50 (65.49)	9.65 (9.96)	10.19 (10.18)	11.45 (11.55)	2.20
H₂L⁴ (C ₁₉ H ₃₄ N ₂ O ₂)	322.49	brown	70	95-97	70-87 (70.76)	10.85 (10.63)	8.75 (8.69)	-	-
[Cu(L⁴)] (C ₁₉ H ₃₂ N ₂ O ₂ Cu)	384.03	blue	40	180	59.45 (59.43)	8.39 (8.40)	7.32 (7.30)	16.61 (16.55)	9.04
[Cu(L⁴)(bipy)] (C ₂₉ H ₄₀ N ₄ O ₂ Cu)	540.22	blue	60	280	64.50 (64.48)	7.43 (7.46)	10.39 (10.37)	12.00 (11.76)	1.80
[Cu(L⁴)(phen)] (C ₃₁ H ₄₀ N ₄ O ₂ Cu)	564.24	blue	80	248	66.02 (65.99)	7.13 (7.15)	9.95 (9.93)	11.00 (11.26)	2.20

*within paranthesis are given the calculated values of the analysis

Results and Discussion

The reactions of 2,4-pentanedione with the alkylene-diamine is represented by equation (1) in Fig. 1. The reaction of the ligands with copper(II) acetate resulted in easy formation of the compounds in moderate to good yields (30-80%). The general equation for the formation of the complexes is represented by equation (2) in Fig. 1. The reaction of the copper(II) complexes with 2,2'-bipyridine, or 1,10-phenanthroline, to give the adducts is represented by equation (3) in Fig. 1. The analytical data, colours, percentage yields, melting points/decomposition temperature (for both ligands and complexes), and room temperature magnetic moments (μ_{eff}) of the complexes are presented in Table 1. The molar conductances of the complexes that dissolved in nitromethane were below $10.00 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ showing that they were non-electrolytes.

Electronic spectra. The diffuse reflectance spectral data for compounds are presented in Table 2. The interpretation of ultraviolet spectra of metal β -detoenolates has been subject to many theoretical models, since experimental studies have not been of great assistance. However, there is consensus that charge transfer bands are in the same region of $\pi\text{-}\pi^*$, with the latter experiencing various splittings (Fackler, 1996). The ultraviolet spectra of the ligands and the complexes displayed three characteristic peaks between 27.7 - 39.9 kK, with an

additional peak also between 40.9 - 48.0 kK. These bands have been assigned to $\pi\text{-}\pi^*$ and charge transfer transitions, respectively. The assignment of d-d transitions for copper(II) complexes is a bit complicated, because of the relatively low symmetry environment (i.e., less than cubic) in which the copper(II) is characteristically found. However, in the cubic environment, the d^9 configurations make the Cu(II) subject to Jahn-Teller distortions, giving rise to unsymmetrical bands, due to a number of overlapping bands (Lever, 1986). Theoretically, upto three transitions can be observed in the visible spectra of copper(II) compounds. Regular tetrahedral derivatives of copper(II) are not common. There is usually a flattening of the tetrahedron leading to a molecule of D_{2d} symmetry, presumably as a result of the Jahn-Teller effect lifting the degeneracy of the 2T_2 ground state. Conversely, clear distinction exists between 4-coordinate, square-planar and tetrahedral geometries. For approximately regular tetrahedral copper(II) complexes, a single broad band in the near infrared region is usually observed with the spectra being blank between 10-20 kK, whereas square-planar complexes absorb in this region (Lever, 1986). All the prepared Cu(II) β -diketoimine complexes had two bands in the ranges of 15.2-15.4 and 18.3-18.7 kK, respectively, and are consequently, 4-coordinate square-planar (Fig. 2a; 3) with the assignment ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions (Lever, 1986). The increase in

Table 2. Some infrared frequencies and electronic transitions for the Cu(II) complexes of tetrodentate β -ketoimines, and their ligands and adduct compounds (cm^{-1})

Compound	$\nu(\text{NH})$	$\nu(\text{C}=\text{O}) + \nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C})$	$\nu(\text{M}-\text{N})$ $\nu(\text{M}-\text{O})$	Electronic transitions ($\times 10^3$)
H_2L^1	3265s	1641s 1538s	-	30.7, 32.3, 39.9
$[\text{Cu}(\text{L}^1)]$	-	1582s 1510s	590m 455m	15.2, 18.5, 30.5, 32.2, 36.2
$[\text{Cu}(\text{L}^1)(\text{bipy})]$	-	1588s 1514s	544m 451s	15.4sh, 18.5, 32.8, 34.1, 41.2
H_2L^2	339m	1600m 1564m	-	30.6, 33.4, 39.6
$[\text{Cu}(\text{L}^2)]$	-	1580m 1522m	570s 466m	15.4, 18.6, 30.8, 34.0, 41.3
$[\text{Cu}(\text{L}^2)(\text{bipy})]$	-	1597m 1561m	546m 406m	14.4sh, 15.7, 36.4, 41.0
$[\text{Cu}(\text{L}^3)(\text{phen})]$	-	1582m 1545m	545m 404m	15.5, 19.2sh, 30.6, 34.3, 42.0
H_2L^3	3436s	1588m 1568m	-	30.7, 33.2, 39.6, 48.0
$[\text{Cu}(\text{L}^3)]$	-	1582m 1520m	557m 455s	15.2, 18.7, 30.5, 34.1, 40.9
$[\text{Cu}(\text{L}^3)(\text{bipy})]$	-	1578m 1515s	544m 425m	14.50sh, 15.7, 34.4, 42.0
$[\text{Cu}(\text{L}^3)(\text{phen})]$	-	1585s 1526s	545m 429m	15.7, 30.8, 37.1
H_2L^4	3420s	1630s 1605s 1564s	-	30.7, 35.6, 41.0
$[\text{Cu}(\text{L}^4)]$	-	1605s 1595s 1562s	533m 407m	15.3, 18.3, 30.6, 34.1, 41.1
$[\text{Cu}(\text{L}^4)(\text{bipy})]$	-	1608s 1596s	564m 427s	14.4sh, 16.0, 30.6, 34.4, 42.0
$[\text{Cu}(\text{L}^4)(\text{phen})]$	-	1586s 1512s	542m 414m	15.5, 19.0sh, 27.7, 31.7, 36.5

s = strong, m = medium, sh = shoulder

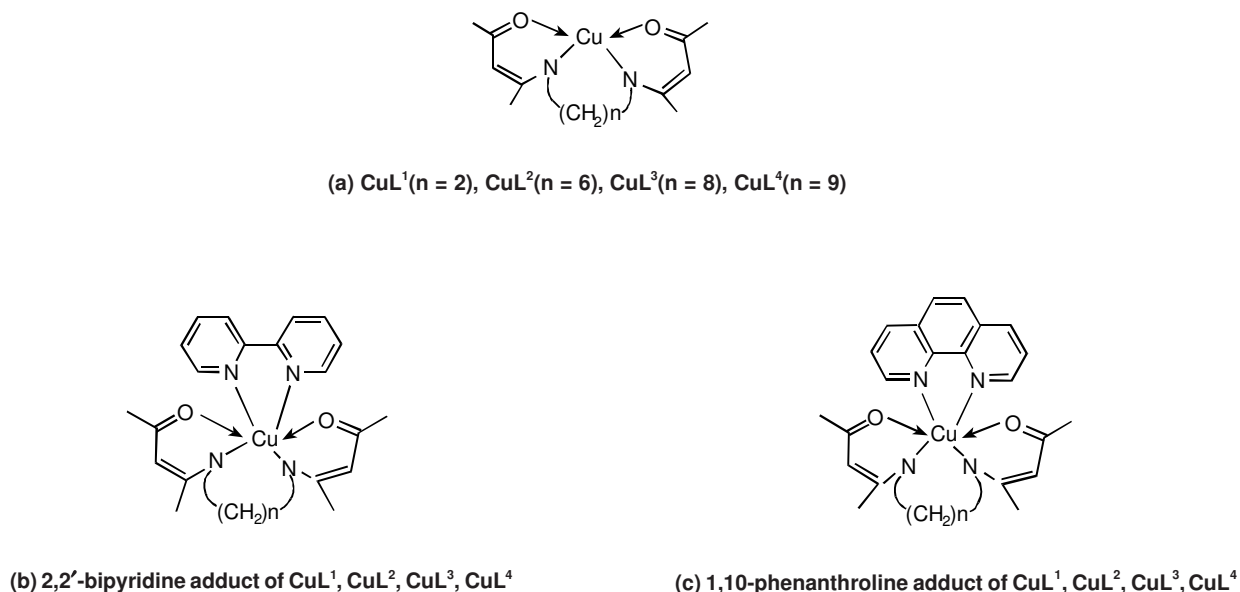


Fig. 2. Suggested structures of: (a) complexes; and (b, c) their adducts.

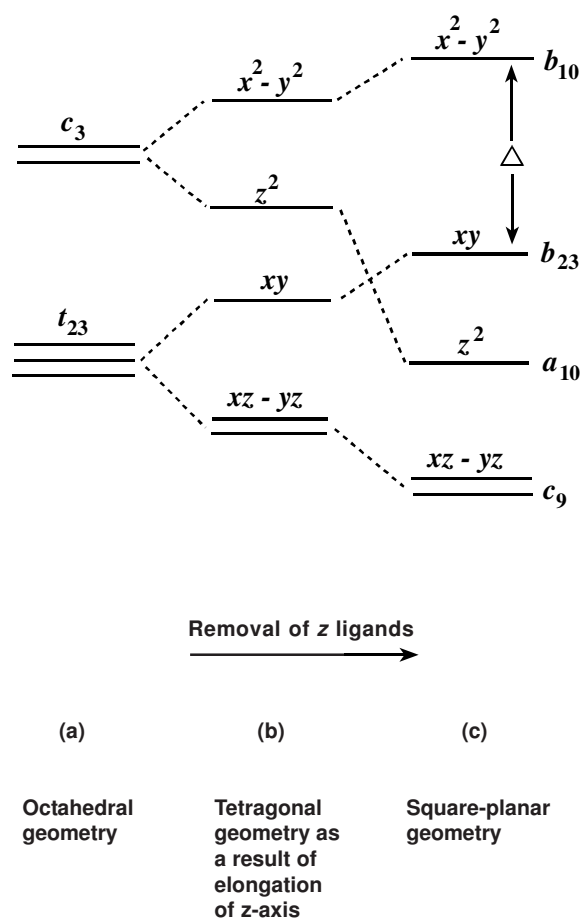


Fig. 3. The energy diagram for square-planar geometry.

methylene chain from $n = 2$ in CuL^1 to $n = 6, 8$ and 9 in CuL^2 , CuL^3 and CuL^4 , respectively, does not have a significant effect on geometry as in their 3-chloro- β -diketoiminate analogs (Osowole *et al.*, 2003). However, this is in contrast to the results of the Ni(II) derivatives where a change of geometry from square-planar to tetrahedral was observed as the length of bridging methylene chain increased (Osowole, 2002). The adducts, however, have different absorption patterns. The compound, $[\text{Cu}(\text{L}^3)(\text{phen})]$, has a single band only at 15.7 kK, while other adducts and $[\text{Cu}(\text{L}^1)(\text{bipy})]$ had single bands at approximately 16.0 kK and 18.5 kK, respectively, with a shoulder at the lower/higher end of the spectrum. The presence of an additional shoulder in some of the adducts is a measure of Jahn-Teller distortion, presumably due to greater flexibility in the longer alkylene-bridge ligands, giving an indication of a six-coordinate octahedral (Fig. 2b; 2c) arrangement of the ligands around the copper ion (Osowole *et al.*, 2003; Patel and Woods, 1990).

Infrared spectra. The relevant infrared vibration bands are given in Table 2. The assignments were made by comparing the spectra of the free ligands with those of the complexes and also with those reported in literature on salicyaldimines, naphthal dimines and 3-chloro- β -ketoamines fluorinated (Osowole *et al.*, 2002; Kabak *et al.*, 1999; Abuhijleh and Ahmed, 1991). The bands around 3265-3436 cm^{-1} are assigned to the $\nu(\text{NH})$ frequency in the ligands, which is an indication of the enolization of the Schiff base, similar to the enolization in β -diketones. The latter band disappears in the spectra of the metal com-

plexes giving an indication of coordination of the amino nitrogen to the copper(II) ion. The series of strong IR bands resulting from uncoordinated C=O, C=N, C=C stretching vibrations appeared coupled between 1538-1641 cm^{-1} , which eventually showed bathochromic shift to 1510-1605 cm^{-1} in the Cu(II) complexes and 1512-1608 cm^{-1} in the adducts. This is indicative of coordination of the copper atom to the nitrogen and oxygen atoms, respectively, in the C=N and the C=O moieties. The hypsochromic shifts of the coupled bands in the adducts relative to the metal complexes, with the exception of [Cu(L³)(bipy)] and [Cu(L⁴)(phen)], is an indication of stronger Cu-N(base) bonds in the adducts. The coupling of different vibrational modes is common in the infrared spectra of metal β -diketonates and β -ketoimines (Osowole *et al.*, 2003; Abd-Elzaher, 2001; Mehta and Desai, 1988; Ueno and Martell, 1956). The bands due to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ were observed at 404-466 and 533-590 cm^{-1} , respectively.

Magnetic moments. The room temperature magnetic moments of copper(II) compounds are expected to be higher than the spin-only value of 1.73 BM as a result of orbital contribution and the spin-orbit coupling, which mixes-in the higher T terms into the ground term. Consequently, a moment of 1.9-2.2 BM is usually observed for mononuclear copper(II) complexes, regardless of the stereochemistry (Earnshaw, 1968). The magnetic susceptibility data of the complexes and adducts studied showed the effective magnetic moments (μ_{eff}) between 1.80-2.20 BM, indicating that they were magnetically dilute with the exception of [CuL³] and [CuL³(bipy)], with moments of 1.66 and 1.57 BM, respectively, which has been attributed to dimerization (Earnshaw, 1968).

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