

Synthesis and Characterization of a New Binucleating Schiff Base Macrocyclic and its Nickel(II) and Copper(II) Complexes

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Abstract

A new binucleating ligand, *m*-xyl-bis(3-bae)) and its copper(II) and nickel(II) complexes have been prepared and characterized by various physical techniques. Data for the complexes indicate that they both have square-planar geometries. High resolution ¹H and ¹³C NMR confirm the square-planar geometry of the binuclear nickel(II) complex is maintained in non-coordinating solvents. The magnetic moment of the copper(II) complex is typical of square-planar complexes and the EPR spectrum in solution indicates the absence of any magnetic coupling between metal centers. In addition, both metal complexes display irreversible electrochemical behavior on various electrode surfaces.

Introduction

There is increasing interest in binuclear complexes which contain ligand structures capable of holding two metal centers in close proximity, while maintaining sufficient flexibility to promote substrate binding. Interest in such complexes arises in part from their potential to function as models of the active site in metalloproteins [1] and to catalyze multielectron redox reactions [2]. The most notable examples of ligands capable of holding two metals at fixed spacial separations are the cofacial diporphyrins [3], cofacial bis(β-diketones) [4], planar polyketones [5] and macrocycles [6], cyclic polyaza compounds [7], 'wishbone' [8] and 'ear muff' [9], and flexible binuclear Schiff base macrocycles [10–13]. The latter class of compounds are of interest to the study described herein because they utilize less motionally restricted ligands to study the effects of metal orientation on electronic, electrochemical, and magnetic properties of the binuclear compounds. Along these lines, Kida and coworkers have prepared and studied a series of 'strati-bis' macrocycles containing 'salen-like' chelates which in several instances display magnetic behavior typical of exchanged

coupled binuclear complexes [10]. Results from their studies suggest that the macrocyclic rings are stacked in a cofacial arrangement resulting in short metal–metal distances and electron delocalization throughout the entire ligand π-system [10]. More recently Eisenberg and coworkers have reported the preparation and characterization of several flexible binuclear Schiff base macrocycles containing derivatives of salprn chelates [12]. These compounds have been designed to bind a single substrate molecule between two electrochemically insulated metal centers and show potential to function as multi-electron redox catalysts. Our work described herein has concentrated on developing new binuclear macrocyclic complexes from more easily prepared polydentate precursors such as bis(β-diketones). We now report the synthesis and characterization of a new xylylene bridging binuclear Schiff base macrocycle and its nickel(II) and copper(II) complexes. The ligand *m*-xyl-bis(3-bae)), along with its binuclear complexes, are shown in Fig. 1, with the appropriate nomenclature used throughout the text.

Experimental

All manipulations were performed under dried-nitrogen using standard Schlenk techniques or in a Vacuum Atmosphere Dry Box. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. and MicAnal Organic Microanalysis, Tuscon, Ariz.

Physical Measurements

¹H and ¹³C NMR spectra were recorded on a Varian XL-300-MHz spectrometer. All chemical shifts are referenced relative to Si(CH₃)₄ in deuteriochloroform (Aldrich) solutions and are reported in ppm. Mass spectra were recorded on a VG 7035 GC-MS mass spectrometer in the EI mode at 70 eV. Infrared spectra were recorded using DRIFTS technique on a Nicolet 9000 FT-IR spectrophotometer using KCl as a diluting matrix. Visible absorption spectra were recorded with a Shimadzu 600 spectrophotometer using quartz cells of 1 cm thickness.

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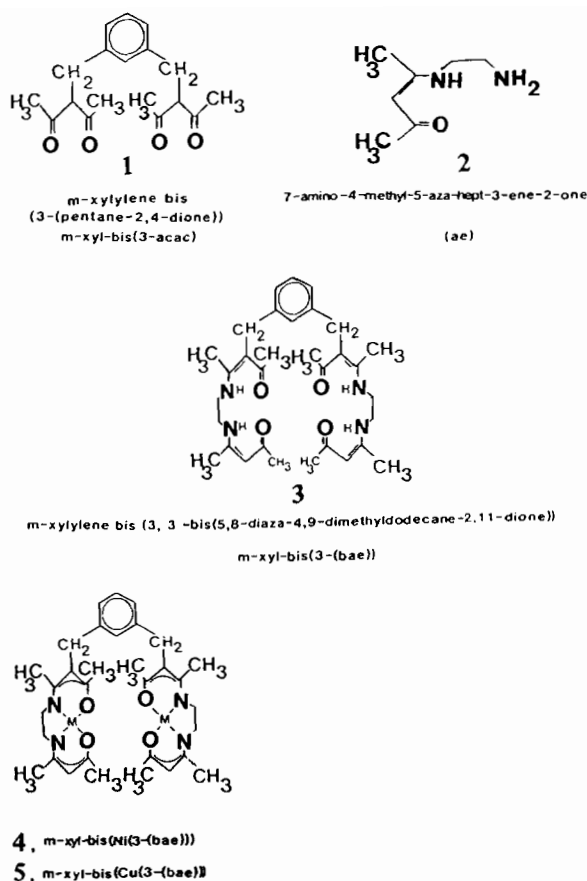


Fig. 1. Ligand and complex labeling schemes and nomenclature.

The solutions were prepared to 0.0010 M concentrations by weight and diluted progressively until the desired concentration for absorption measurements was obtained. Spectroscopic grade dichloromethane (Baker) was used as a solvent for all measurements. Extinction coefficients are reported in units of $M^{-1} \text{ cm}^{-1}$. Room temperature solid state magnetic susceptibilities were recorded on a PAR Model 155 Vibrating Sample Magnetometer which has been calibrated with $\text{HgCo}(\text{NCS})_4$. Pascal constants were used to correct all data for diamagnetism [14]. EPR spectra were recorded on a Varian E-109 spectrometer equipped with an Oxford Instruments, Inc. cryostat. Spectra were recorded in dichloromethane and/or toluene solutions. Electrochemical measurements were made at room temperature using a PAR 173 potentiostat, a PAR 175 universal programmer, a PAR 179 digital coulometer and a Houston Instruments Model 2000 X-Y recorder. A conventional three-electrode cell used in the study consisted of a saturated calomel (SCE) reference electrode, a platinum coiled auxiliary electrode and a platinum or glassy-carbon working electrode.

Melting points were determined using a Thomas Hoover capillary melting point apparatus. All values recorded are uncorrected.

Reagents

All solvents used were reagent grade and were dried by standard literature methods prior to use. Tert-butyl alcohol was dried and distilled from KOH and used immediately.

Ethylenediamine and α, α' -dibromo-*m*-xylene were purchased from Aldrich and used without further purification. Potassium tert-butyl oxide was purchased from Aldrich and handled in the dry-box. Pentane-2,4-dione was purchased from Matheson and Bell and distilled prior to use. Copper(II) and nickel(II) acetate dihydrates were purchased from Merck and used as received.

Synthesis of Ligands and Complexes

m-Xylylene bis(3-(pentane-2,4-dione))-*m*-xylyl-bis(3-acac) (1)

Compound 1 was prepared following procedures reported previously by Martin *et al.* [15]. The resulting oil crystallizes from ethanol after a month at -10°C yielding colorless crystals in 41% yield, melting point (m.p.) 108°C (110°C [15]). *Anal.* Calc. (Found): C, 71.25 (70.78); H, 7.31 (7.26)%. Mass spectra (303 g mol^{-1} , m/z): $303(\text{M}^+, 3)$ $203(10)$, $100(26)$, $85(100)$, $43(95)$. ^1H (CDCl_3 , δ): 2.02(s, 12H); 3.61(s, 4H); 6.96–7.21(m, 4H). IR (KCl, cm^{-1}): $\nu(\text{C}=\text{O})$ 1605 cm^{-1} .

7-Amino-4-methyl-5-aza-hept-3-ene-2-one (ae) (2)

Compound 2 was prepared following a modified procedure of Kwiatkowski and Kwiatkowski [16]. Pentane-2,4-dione (25 ml, 242 mmol) was added dropwise to a stirred absolute ethanol solution (200 ml) containing 50 ml (748 mmol) of ethylenediamine at 0°C . After addition of the β -diketone was complete the solution was stirred for 15 min. The solvent was then removed *in vacuo* yielding a yellow oil. The oil was distilled immediately under vacuum at $110\text{--}112^\circ\text{C}$ (2 mm/Hg), yielding approximately 13.2 g (33%) of the highly viscous colorless liquid 2. ^1H NMR (CDCl_3 ; δ): 1.93(bs, 2H); 1.67(s, 3H); 1.71(s, 3H); 2.60(t, 2H); 3.02(t, 2H); 4.71(s, 1H); 10.68(bs, 1H).

m-Xylylene bis(3,3'-bis(5,8-diaza-4,9-dimethyldodecane-2,11-dione)) *m*-xylyl-bis(3-bae)) (3)

Compound 1 (300 mg, 0.998 mmol) was dissolved in 25 ml of dichloromethane and added to a 25 ml solution of dichloromethane containing 282 mg (2.00 mmol) of 2. The resulting homogeneous yellow solution was then warmed to 50°C with rapid stirring for 16 h. The solution was cooled

to room temperature and dried with anhydrous MgSO_4 , then filtered. The solvent was removed under vacuum resulting in a colorless oil which crystallized as an off-white powder from an ethanol/ether solution over a period of 1–2 days at -10°C (30%), m.p. 114°C . *Anal.* Calc. (found) for $\text{C}_{32}\text{H}_{46}\text{O}_4\text{N}_4$: C, 69.79(69.41); H, 8.42(8.56); N, 10.17(10.00)%. Mass spectrum (550 g mol^{-1} , m/z): 551($\text{M} + 1^+$, 3); 507(17); 272(22); 125(32); 112(100); 98(42); 82(56). $^1\text{H NMR}$ (CDCl_3 , δ): 1.84(s, 6H); 1.90(s, 6H); 1.94(s, 6H); 2.01(s, 6H); 3.43(t, 8H); 3.54(s, 4H); 4.86(s, 2H); 6.96–7.21(m, 4H); 10.88(bs, 2H); 12.35(bs, 2H). IR(KCl, cm^{-1}): $\nu(\text{C}=\text{O})$ 1606, 1580 cm^{-1} .

m-Xyl-bis(Ni(3-(bae))) (4)

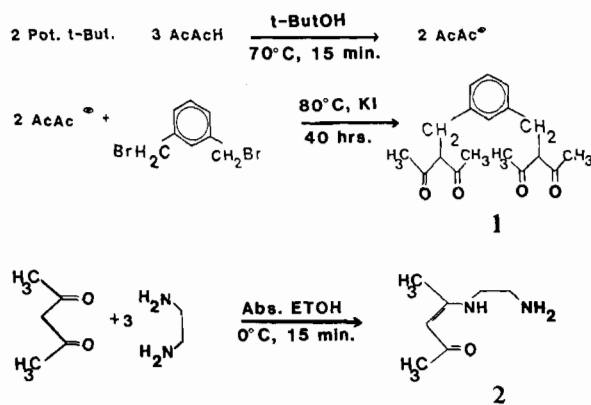
A 0.110 g (0.200 mmol) amount of 3 is dissolved in 15 ml of methanol under a dry nitrogen atmosphere. To the solution is added with stirring 0.100 g (0.500 mmol) of nickel(II) acetate dihydrate dissolved in 25 ml of hot methanol. The reaction mixture is warmed to 50°C and stirred for 2 h at which time the solvent is removed *in vacuo*, yielding a red-brown oil. The oil is redissolved in dichloromethane and filtered to remove excess nickel(II) acetate. The filtrate is dried with MgSO_4 and the solvent removed *in vacuo*. To the resulting viscous oil is added 2 ml of diethyl ether. Removal of the ether *in vacuo* results in a red-brown solid which is dried *in vacuo* for several hours, yielding 4 (86%), m.p. $>50^\circ\text{C}$. m.p. dec. 147°C . *Anal.* Calc. (found) for $\text{C}_{32}\text{H}_{42}\text{O}_4\text{N}_4\text{Ni}_2$: C, 57.87(57.90); H, 6.37(6.68); N, 8.44(8.58); Ni, 17.68(17.54)%. IR(KCl, cm^{-1}): $\nu(\text{C}=\text{O})$ 1560 cm^{-1} , $\nu(\text{C}=\text{N})$ 1510 cm^{-1} . UV-Vis [CH_2Cl_2 ; λ_{max} (nm), (ϵ ($\text{M}^{-1}\text{cm}^{-1}$))]: 567(112). $^1\text{H NMR}$ (CDCl_3 , δ): 1.84(s, 6H); 1.88(s, 6H); 1.92(s, 12H); 3.50(t, 8H); 3.57(s, 4H); 4.90(s, 2H); 6.96(m, 4H).

m-Xyl-bis(Cu(3-(bae))) (5)

Compound 5 is made following the same procedure used to prepare 4, except substituting copper acetate dihydrate for the metal salt. A purple solid is isolated in 76% yield, m.p. dec. 143 – 146°C . *Anal.* Calc. (found) for $\text{C}_{32}\text{H}_{42}\text{O}_4\text{N}_4\text{Cu}_2$: C, 57.05(56.73); H, 6.28(6.36); N, 8.31(7.99); Cu, 18.85(19.01)%. IR(KBr, cm^{-1}): $\nu(\text{C}=\text{O})$ 1570 cm^{-1} , $\nu(\text{C}=\text{N})$ 1506 cm^{-1} . UV-Vis [CH_2Cl_2 ; λ_{max} (nm), (ϵ ($\text{M}^{-1}\text{cm}^{-1}$))]: 547(364) and 656sh(196).

Mass Spectrometry

The mass spectrum of 3 was obtained using a VG 7035 mass spectrometer (Director: Professor William Pierce) in the Department of Pharmacology at the University of Louisville, Louisville, Ky. The instrument was operated in the positive ion mode and an electron ionization of 70 eV was employed. All scans were obtained for the range of $m/z =$



Scheme 1.

44–600, at a source temperature of 150°C and an acceleration potential of 4 kV.

Approximately 0.5 mg of sample were dissolved in methanol and slowly applied to the platinum wire of the desorption probe under a stream of warm air. The probe was inserted directly into an ion source for analysis.

For compound 1 the relative abundance for $m/z = 303(\text{M}^+)$ ion is 3 ± 1 as determined from the average of 5 determinations. For compound 3 the relative abundance for $m/z = 550(\text{M})^+$, $551(\text{M} + 1)^+$, and 552 are 100, 38 and 8, respectively. An exact mass has been determined to be 550.352 (calc. 550.492) g mol^{-1} . Other prominent peaks observed are $m/z = 507(\text{M} - 43, \text{acyl})$, $438(\text{M} - 112)$, $225(\text{M} - 225)$ and $112(\text{M} - 438)$. See also 'Supplementary Material'.

Results and Discussion

Ligand Synthesis and Characterization

The binucleating ligand *m*-xyl-bis(3-(bae)) (3) has been prepared following the procedure outlined in Schemes 1 and 2. Starting compound 1 and 2, are prepared from slightly modified procedures published previously by others. Infrared and proton NMR spectra of compounds 1 and 2 are consistent with their proposed structures and agree well with the data reported in the literature. Condensation of two equivalents of 2 with one equivalent of 1 in dichloromethane affords 3 in reasonable yields, after recrystallization from ethanol/ether solutions. The off-white solid of 3 is analytically pure and has been characterized by IR, mass spectrometry (see 'Experimental') and ^1H and ^{13}C NMR. The infrared spectrum of 3 shows two strong but broad absorption bands at 1606 and 1580 cm^{-1} which are assigned to the $\nu(\text{C}=\text{O})$ stretching modes of the molecule. A broad band at 1608 cm^{-1} has been reported for bis(acetylacetone)ethylenediamine (bae) (I) [16].

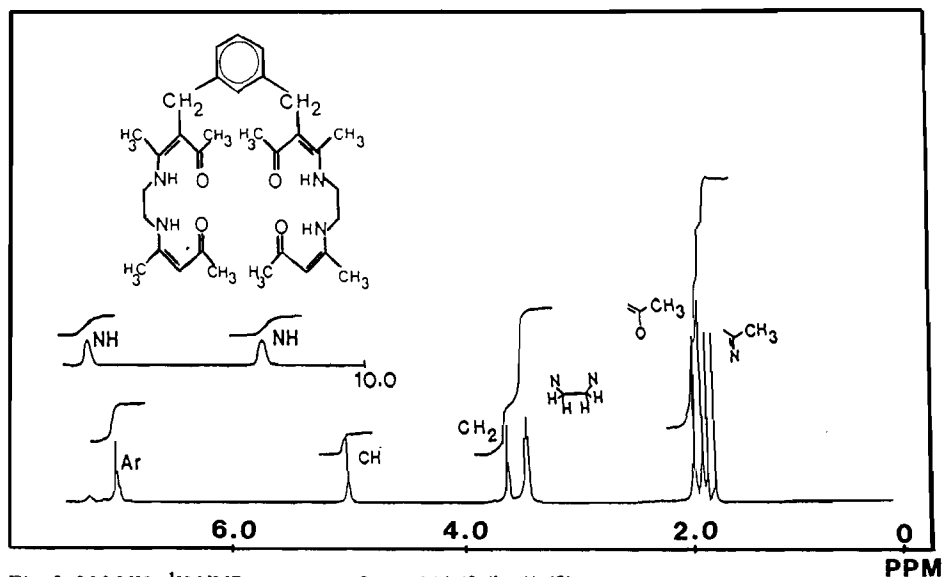
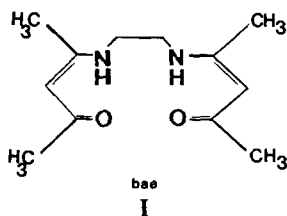


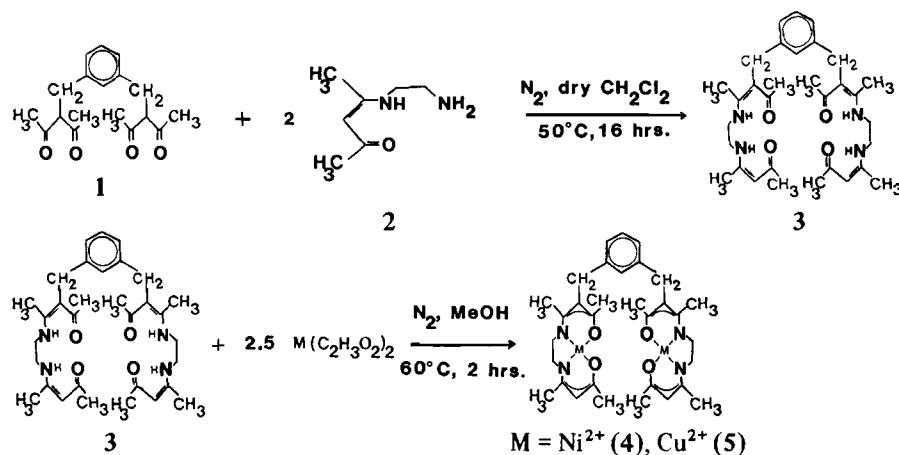
Fig. 2. 300 MHz ^1H NMR spectrum of *m*-xylyl-bis(3-(bae)) (3).



This absorption has been attributed to the carbonyl stretch of the ketoamine form of the molecule. The IR spectrum of **3** also contains a broad absorption at 3145 cm^{-1} which is assigned to the hydrogen bonded amino group indicating that the structure of **3** is best described by the ketoamine form of the ligand depicted in Fig. 1.

The 300 MHz proton NMR spectrum of *m*-xylyl-bis(3-(bae)) (**3**) is shown in Fig. 2 and relevant data with respective assignments are summarized in Table I. In the proton spectrum of **3** four distinct

singlets are observed at 1.84, 1.90, 1.94 and 2.01 ppm which are assigned to the four inequivalent methyl groups on the chelate ring. The inequivalence of the methyl protons arises from the lack of symmetry in the bae units due to substitution at only one of the γ -positions of each ring. The methylene hydrogens of the ethylenediamine rings appear as a broadened triplet at 3.43 ppm. The vinylic CH and benzylic CH_2 protons appear as singlets at 4.86 and 3.58 ppm, respectively. A comparison of the relative intensities of the vinylic:benzylic:methylene-(ethylenediamine) resonances indicates that these protons are present in the expected 1:2:4 ratios consistent with the structure proposed in Fig. 1. The aromatic protons appear as a series of multiplets of area four in the 6.96–7.12 ppm region. Finally, there are two sets of NH resonances, each of area two at 10.88 and 12.35 ppm. For bae, the NH protons are observed at 10.86 ppm in CDCl_3 . There-



Scheme 2.

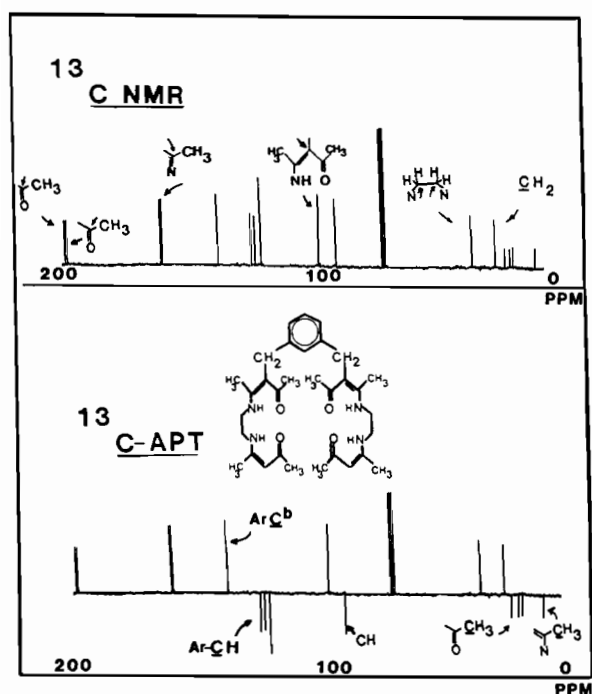


Fig. 3. 22.5 MHz ^{13}C and APT spectra of *m*-xyl-bis(3-(bae)) (3).

TABLE I. 300 MHz ^1H NMR Chemical Shifts^a δ (ppm) for Compounds 3 and 4

Proton Chemical shift (ppm/TMS)

Proton	Chemical shift (ppm/TMS)	Chemical shift (ppm/TMS)
	2.01s, 1.94s	1.92s
	1.90s, 1.84s	1.88s, 1.84s
CH	4.86s	4.90s
	3.43t	3.50t
NH	10.88s, 12.35s	not present
Ar	6.96m	6.96m
Ar-CH ₂	3.58s	3.57s

^aAll measurements are recorded in CDCl_3 solutions and are reported relative to TMS (s = singlet, t = triplet, m = multiplet).

fore, the resonance at 10.88 ppm in the ^1H NMR spectrum of compound 3 can be assigned to the NH protons associated with the unsubstituted portion of bae unit. The downfield shift of the additional set of NH protons reflects the presence of the electron withdrawing benzylic functionality on the chelate ring. The chemical shifts reported in Table I are in agreement with data reported elsewhere for bae [17].

The ^{13}C and APT NMR spectra of compound 3 are shown in Fig. 3. A summary of the data along with respective assignments are listed in Table II. Seventeen resonances are observed in the ^{13}C spectrum of 3 which is consistent with the structure proposed in Fig. 1. The unsymmetrical nature of the bae chelates is confirmed by the presence of two different carbonyl and enamine carbon atoms at 196.1, 196.9 and 163.4, 164.0 ppm, respectively, in addition to the presence of two different γ -carbon atoms in the ring at 96.8 (unsubstituted) and 102.8 (substituted) ppm. The bridging ring methylene carbon atoms are slightly inequivalent, appearing at 43.8 and 44.4 ppm. These results are in agreement with the data reported for bae [17].

Data obtained from the APT experiment on 3 is illustrated in Fig. 3. This pulse routine allows

TABLE II. 22.5 MHz ^{13}C NMR Chemical Shifts^a δ (ppm) for Compounds 3 and 4

Carbon	<i>m</i> -xyl-bis(3-(bae)) Chemical shift (ppm/TMS)	<i>m</i> -xyl-bis[Ni(3-(bae))] Chemical shift (ppm/TMS)
	29.0, 30.6	24.6, 29.6
	18.8, 28.4	18.8, 21.0
CH	96.8	99.6
	43.8, 44.4	52.8, 54.4
	196.1, 196.9	175.0, 176.8
	163.4, 164.0	164.6, 166.4
Ar-CH	133.3, 127.7, 125.3	128.6, 127.2, 125.2
Ar-C ^b	144.0	141.6
CH ₂	34.8	35.6
	102.8	104.4

^aSpectra recorded in CDCl_3 relative to TMS as an internal standard. ^bQuarternary ring carbon atom.

definitive assignment of each carbon nucleus in compound **3**. Carbon atoms bonded to odd numbers of hydrogen atoms are inverted while those bonded to even numbered hydrogen nuclei remain upright. Therefore, in compound **3** the aromatic CH, vinylic CH and methyl carbon atoms invert while the quarternary and methylene carbon atoms remain upright. Again evidence supporting substitution at only one of the ring γ -positions on each chelate ring is shown by the inversion of only the vinylic CH carbon atoms and retention of orientation of the substituted quarternary γ -carbon atoms. The detailed assignment of both the proton and carbon-13 resonances gives conclusive evidence for the bis-macrocyclic structure of compound **3**.

Characterization of Nickel(II) and Copper(II) Complexes

m-Xyl-bis[Ni(3-(bae))]

Compound **4** is prepared by the reaction of nickel(II) acetate with **3** in warm methanol solutions and is isolated as a red-brown microcrystalline solid in 86% yield. The elemental analysis of the binuclear complex is satisfactory and the compound is soluble in most common organic solvents, giving yellow to light brown solutions. Crystals suitable for X-ray crystallographic analysis have not been obtained to date. The infrared spectrum of **4** shows two strong but broad absorptions at 1560 and 1510 cm^{-1} which are attributed to the C=O and C=N stretching modes of the molecule. Similar spectral properties have been reported for other nickel(II) Schiff base macrocycles [18, 19]. The visible absorption spectrum of **4** is consistent with a square-planar arrangement of the N_2O_2 donor atoms around each nickel(II) ion. A maximum in the absorption spectrum occurs at 567(112) nm (Fig. 4). Compound **4** exhibits an irreversible two-electron reduction wave at -1.83 V versus SCE in DMF at glassy carbon electrodes and an irreversible wave at nearly the same potential at platinum.

Compound **4** is diamagnetic in the solid-state and in deuteriochloroform solutions. The 300 MHz proton NMR spectrum of **4** is similar to that of the free ligand, shown in Fig. 1. A complete list of relevant chemical shifts for compound **4** is reported in Table I. The ring methylene, benzylic and vinylic protons are observed at 3.57, 3.50 and 4.90 ppm in the expected 4:2:1 ratios of intensities. In addition, there are no resonances downfield of the aromatic protons centered at 6.96(4H). The absence of NH resonances in the proton spectrum is conclusive evidence that the nickel(II) ions are coordinated to **3**. The structure of **4** is further supported by the ^{13}C results reported in Table II. When **3** coordinates to the nickel(II) ion the chemical shifts of the various carbon atoms change in a way which is consistent with the data reported for Ni(II)(bae) [20].

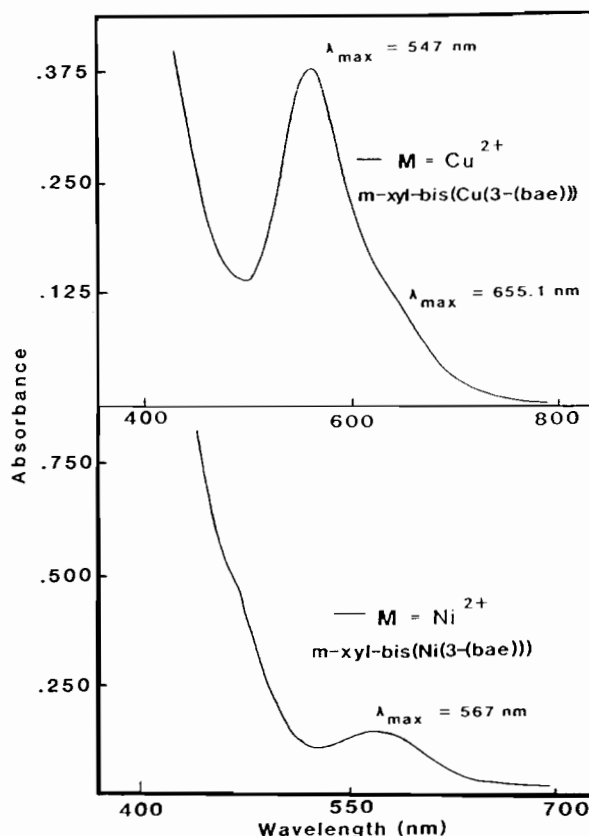


Fig. 4. Electronic spectra of compounds **4** and **5** in CH_2Cl_2 (approximate concentrations of 1×10^{-3} M).

m-Xyl-bis[Cu(3-(bae))]

Compound **5** is prepared by the reaction of **3** with copper acetate in warm methanol solution and is obtained as a purple solid in 76% yields. Isolation of the compound is accomplished with little difficulty from ether solutions. Unfortunately, crystals suitable for X-ray crystallographic analysis have not yet been obtained. The binuclear complex analyzes correctly and like the nickel(II) complex is soluble in most common organic solvents. The infrared spectrum of **5** displays broad absorptions near 1570 and 1506 cm^{-1} assigned to the stretching vibration of the C=O and C=N bonds, respectively. Comparable stretching frequencies are reported for the C=O and C=N bonds in Cu(bae) [17]. The electronic spectrum of **5** is typical of square-planar copper(II) complexes and shows a $\lambda_{\text{max}} = 547(364)$ nm with a shoulder at 635(196) nm, in dichloromethane (Fig. 4). The solid-state spectrum agrees with the results obtained in solution indicating that there is no change in coordination geometry as a result of solvent interactions. For Cu(bae), in chloroform, a maxima in the absorption spectrum is observed at 543(112) nm and a shoulder at 635 nm [17]. Compound **5** also exhibits irreversible electro-

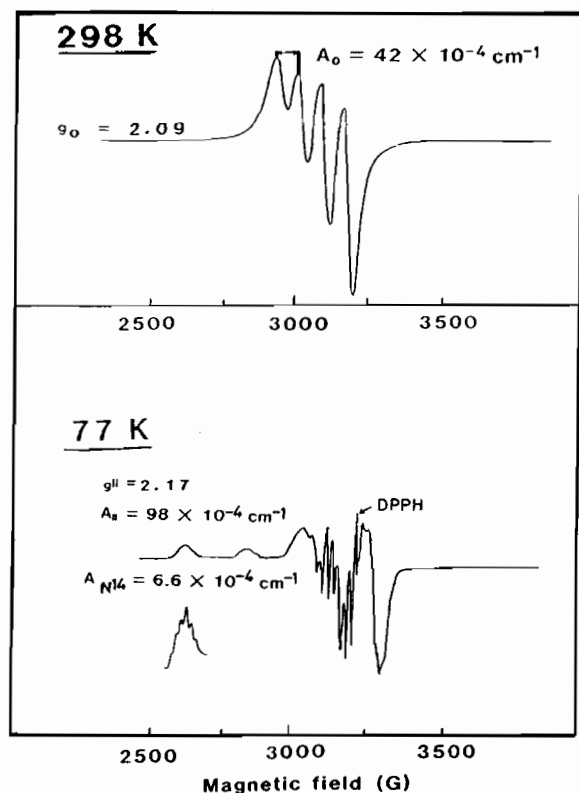


Fig. 5. EPR spectra of *m*-xy-bis[Cu-(3-bae)] (5) recorded in $C_6H_5CH_3$ at 295 and 77 K.

chemical properties in both CH_2Cl_2 and DMF reducing at -1.76 V versus SCE at a glassy carbon electrode. Cu(bae) on the other hand, undergoes one electron reduction at -1.75 V versus SCE. The origin of the irreversible reduction of 5 is under further investigation.

The binuclear copper complex 5 is paramagnetic both in the solid-state and in solution. The room temperature effective magnetic moment of 5 as a solid is $\mu_{\text{eff}} = 1.95$ BM/Cu center which is consistent with other square-planar copper(II) complexes [21]. The X-band EPR spectrum of the powdered complex shows evidence of magnetic exchange couplings between metal centers. A broad featureless signal corresponding to $\Delta M_s = 1$ transitions is centered at 3110 G in addition to a weak signal at 1554 G, which is associated with the $\Delta M_s = 2$ transition arising from the coupling between $S = 1/2$ metal ions. In the absence of structural data on 4 the exact origin of the exchange interaction is unknown. A direct intradimer metal-metal interaction seems unlikely due to the >4.0 Å separation between the macrocycle rings in the *syn* conformation as estimated from CPK models. Reduced magnetic moments for similar binuclear salprn Schiff base complexes have been reported recently by Eisenberg *et al.* indicating the presence of exchange coupling

in solution [12]. An alternative view of the origin of the exchange coupling observed for 4 may involve macrocyclic pairing of adjacent binuclear complexes in solids. Similar behavior has been reported for Cu(salen) which displays a 'normal' magnetic moment at room temperature but an EPR spectrum containing features characteristic of a binuclear system [22].

At ambient temperatures, CH_2Cl_2 or $C_6H_5CH_3$ solutions of 4 give isotropic spectra with a four-line pattern ($g_0 = 2.09$, $|A_0| = 42 \times 10^{-4} \text{ cm}^{-1}$) indicative of planar, monomeric Cu^{2+} (Fig. 5). No ligand hyperfine structure could be resolved in either solvent system. Apparently the complex exists as a magnetic non-coupled dimer in non-coordinated solvents at room temperature. In either solvent the spectrum of 5 at 77 K is consistent with a monomeric environment around each metal center ($g_{\parallel} = 2.17$ and $A_{\parallel} = 98 \times 10^{-4} \text{ cm}^{-1}$). No half-field signal is observed in either solvent. Five lines are clearly resolved on the perpendicular component, with an average spacing of $6.6 \times 10^{-4} \text{ cm}^{-1}$ indicating that the unpaired electron is interacting with two nitrogen nuclei. From the data one may conclude that the copper(II) centers in 5 remain magnetically uncoupled in solution at both room and liquid nitrogen temperatures.

Conclusions

A new binucleating Schiff base macrocycle ligand has been prepared and characterized. The ligand forms stable metal complexes with nickel(II) and copper(II) ions and both compounds are square-planar in the solid-state and in non-coordinating solvents. All attempts to obtain single crystals suitable for X-ray crystallographic studies have failed; however, the complexes have been characterized completely by conventional analytical and spectroscopic techniques.

The visible electronic and infrared spectra of both the binuclear nickel(II) and copper(II) complexes are very similar to the spectra of the mononuclear analogues of bae. Cyclic voltammetry of both the nickel(II) and copper(II) complexes display irreversible reduction waves in DMF. From the EPR spectrum in non-coordinating solvents the binuclear Cu(II) complex appears to be electronically insulated. No exchange interaction was detected as in a variety of organic solvents, indicating that the copper(II) centers are not magnetically coupled. Attempts to determine the flexibility of the binuclear system through formation of adducts, bridging both metal centers, are in progress. Finally, we have extended our studies to a similar class of binuclear Schiff base macrocycles which have been synthesized from α -bridged bis(β -diketones). The results of these studies will be reported elsewhere.

Supplementary Material

A complete mass spectrum of compound 3 is available upon request from the authors.

Acknowledgements

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