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Binuclear Schiff Base Complexes

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Abstract

Two new binucleating ligands, pentyl-bis(3-(bae)) and octyl-bis(3-(bae)) and their copper(II) and nickel(II) complexes have been prepared and characterized. The binuclear Cu(II) and Ni(II) complexes display magnetic and spectroscopic behavior characteristic of square-planar monomeric compounds. No magnetic exchange interactions between copper centers was detected at either room or liquid nitrogen temperatures. Both of the Cu(II) and Ni(II) ions in these complexes undergo two quasi-reversible one-electron reductions at nearly the same potentials.

Introduction

There has been much interest recently in binucleating ligands that hold two metal ions in close proximity [1–15]. The focus of some of these studies has been directed towards understanding the structural and electronic factors regulating multielectron transfer processes [2]. In addition, much effort has focused on developing inorganic model compounds that mimic in part some of the unique spectral, magnetic and redox properties of metalloproteins [3]. Numerous binucleating ligands have been employed in these and related studies [4–15]. Ligands that provide a motionally less restrictive coordination environment are of interest because they offer greater potential for exploring the effect of metal orientation on electronic, electrochemical and magnetic properties of binuclear systems. We are interested in developing new binucleating ligands that may function as multielectron redox reagents via formation of donor–acceptor complexes between electrochemically insulated metal centers. Such compounds could in principle function as multielectronic 'receptor units' [16] exchanging several electrons in a narrow potential range.

Understanding the factors regulating cooperativity between metal centers in binuclear complexes during electron transfer is fundamental to our understanding of more complex multielectronic processes found in metalloproteins, such as: the Type III copper proteins hemocyanin, tyrosinase, and lacase [3c]. The copper(II) centers in these proteins are known to undergo reduction to Cu(I) in two rapid monoelectronic steps at identical potentials [17]. Several inorganic model compounds duplicate this electrochemical behavior [8b, c, 16] but the structural and electronic factors regulating biological electron transfer reactions still are poorly understood. In a previous paper [18], we described our initial efforts at developing binucleating Schiff base complexes from easily prepared polydentate bis(β-diketone) ligands. We now report the results of our latest study utilizing α-branched bis(β-diketones) to prepare bimetallic complexes. The synthesis and characterization of two new binuclear Schiff base complexes and their nickel(II) and copper(II) complexes are described herein. The ligands pentyl-bis-(1-bae)) and octyl-bis-(1-bae)) along with their metal complexes are illustrated in Fig. 1 along with the appropriate nomenclature used throughout the text.

Experimental

Reagents

All solvents used were reagent grade and dried using standard literature procedures. Sodium amide, 1,3-dibromopropane, 1,6-dibromohexane, and ethylenediamine were purchased from Aldrich and used without further purification. Pentane-2,4-dione was obtained from Matheson and Coleman and distilled prior to use. Copper(II) and nickel(II) acetate dihydrates were used as received from Merck. Cu(bae) and Ni(bae) were prepared by published procedures [19].

Physical Measurements

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN and Desert Analytics Organic Microanalysis, Tucson, AR. Infrared spectra for all complexes were obtained using the

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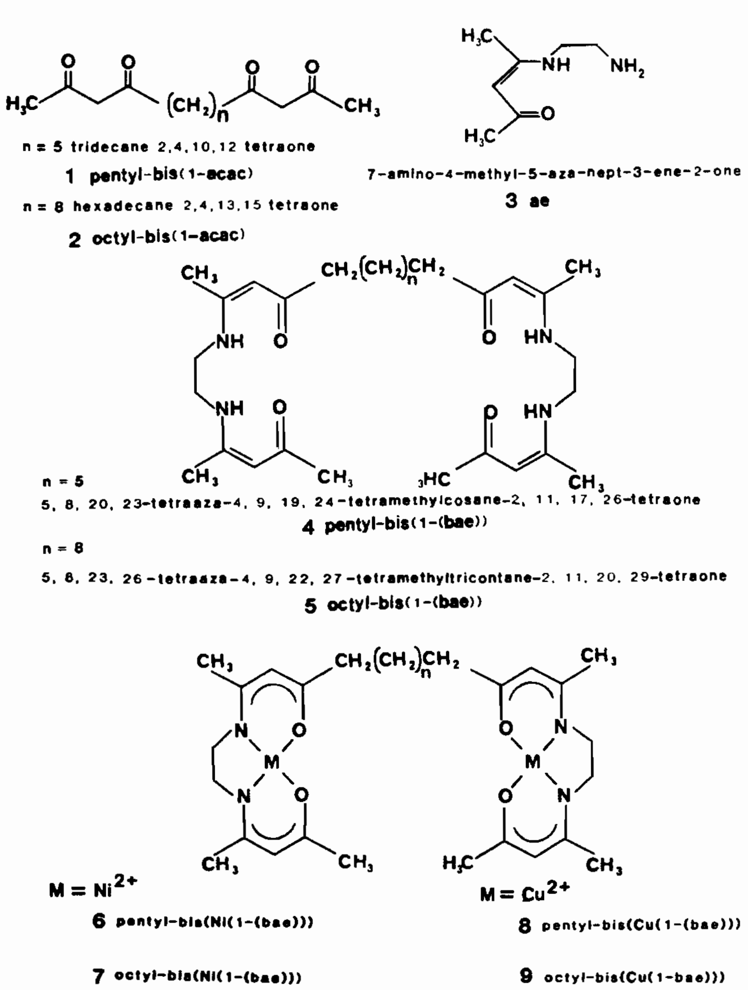


Fig. 1. Nomenclature and labeling schemes for ligands and metal complexes.

'DRIFTS' mode on a Nicolet 9000 FT-IR spectrophotometer. The visible absorption spectra for the metal complexes were recorded in dichloromethane using a Shimadtzu 600 spectrophotometer. The ^1H and ^{13}C NMR spectra for all compounds were recorded in $CDCl_3$ using a Varian XL-300 MHz spectrometer with chemical shifts reported in ppm (δ units) relative to $(CH_3)_4Si$.

The mass spectra of compounds were obtained using a VG 7035 mass spectrometer. (Director: Dr William Pierce, Department of Pharmacology, University of Louisville.) About 0.5 mg of sample dissolved in methanol were applied to a platinum wire and after evaporation the probe and sample were inserted directly into an ion source. The instrument was operated in the positive ion mode with an electron ionization of 70 eV. All scans were recorded in the range of m/z = 44–600, at a source temperature of 150 °C and an acceleration potential of 4 KV. Each compound displays a molecular ion consistent with the proposed molecular formula. See 'Supplementary Material'.

A Hoover capillary melting point apparatus was used to record uncorrected melting and decomposition points. Room temperature solid-state magnetic susceptibilities were recorded on a PAR Model 155 Vibrating Sample Magnetometer which has been calibrated with $HgCo(NCS)_4$. Pascal constants were used to correct all data for diamagnetism [20]. EPR spectra at room temperature and of frozen solutions of the copper(II) complexes in dichloromethane and/or toluene were obtained using a Varian E-109 spectrometer equipped with an Oxford Instruments, Inc. cryostat. Frozen solution EPR spectra were recorded at 77 K and g values for each complex were evaluated using DPPH as a reference. Electrochemical measurements were made at room temperature using a PAR 173 potentiostat, a PAR 175 universal programmer, a PAR digital coulometer and Houston Instruments 2000 X-Y recorder. A conventional three-electrode cell was employed in all measurements which consisted of a Ag/AgCl reference electrode, a coiled platinum wire auxiliary electrode, and a glassy carbon working electrode. All voltammograms were recorded in DMF under a nitrogen atmosphere using tetra-n-butylammonium perchlorate (0.1 M) as the supporting electrolyte.

Synthesis of Ligands

The general procedure for synthesis of the linear bis-β-diketones, compounds **1** and **2**, has been reported previously by Hampton *et al.* [21]. We have used a modification of this procedure in our study [22].

Tridecane-2,4,10,12-tetraone (pentyl-bis(1-acac)) (1)

The disodium salt of pentane-2,4-dione was prepared by placing 500 ml of liquid ammonia, 52.1 g (1.34 m) sodium amide and 67.5 g (0.668 m) pentane-2,4-dione in 20 ml of ether in a 1 liter three-neck flask under nitrogen at –78 °C. To this solution was added 63.2 g (0.313 m) of 1,3-dibromopropane in 20 ml of diethyl ether over a 30 min period after which time it was stirred for 2 h. Approximately 100 g of crushed ice and 70 ml of concentrated HCl in 200 ml of diethyl ether were added slowly. The organic phase was separated, dried with $MgSO_4$, and the solvent removed in vacuum. Crystallization of the resulting oil from ethanol produced 45 g (60%) of pentyl-bis(1-acac) (**1**). Melting point (m.p.) = 68 °C (lit. 66–67) [21]. *Anal.* Calc. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.98; H, 8.56%. Mass spectrum (240 g mol^{-1} *m/z*; 241(m + 1^{1+}, 1.85); 141(13); 113(29). ^{1}H NMR ($CDCl_3$, δ): 1.30(m, 2H); 1.60(p, 4H); 2.03(s, 6H); 2.25(t, 4H); 3.55(s, 0.5H) keto; 5.47(s, 1.5H) enol; 15.50(s, 2H). IR (KCl, cm^{-1}): ν(C=O) 1610 cm^{-1}.

Hexadecane-2,4,13,15-tetraone (octyl-bis(1-acac)) (2)

Compound 2 is prepared by the procedure described above except 1,6-dibromohexane was substituted for the 1,3-dibromopropane. Crystallization from ethanol yielded 56 g (65%) of **2**, m.p. = 80 °C (lit. 78–81). *Anal.* Calc. for $C_{16}H_{26}O_4$: C, 68.09; H, 9.22. Found: C, 68.10; H, 9.35%. Mass spectrum: (282 g mol^{-1}, *m/z*); 283(m + 1^{1+}, 1.0); 279(5); 246(2); 183(26); 113(29); 100(51); 55(12). ^{1}H NMR ($CDCl_3$, δ): 1.27(m, 8H); 1.56(p, 4H); 2.03(s, 6H); 2.23(t, 4H); 3.55(s, 0.5H) keto; 5.47(s, 1.5H) enol; 15.52(s, 2H). IR (KCl, cm^{-1}): ν(C=O) 1610 cm^{-1}.

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

Compound 3 was prepared following a modified procedure of Kwiatkowski *et al.* [23]. Pentane-2,4-dione (25 ml, 242 mmol) was added dropwise to a stirred absolute ethanol solution (200 ml) containing 50 ml (748 mol) 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 110–112 °C (2 mm/Hg), yielding approximately 13.2 g (33%) of the highly viscous colorless liquid **2**. ^{1}H 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).

5,8,20,23-Tetraaza-4,9,19,24-tetramethylcosane-2,11,17,26-tetraone (pentyl-bis(1-(bae)) (4)

3.10 g (0.0129 m) of pentyl bis(1-acac) (**1**) were dissolved in 25 ml of dichloromethane in a 2-neck round bottom flask and added to a 25 ml solution of dichloromethane containing 3.67 g (0.0260 m) of **3**. The resulting homogeneous yellow solution was then warmed to 50 °C with stirring for 14 h. The solution was cooled and dried with $MgSO_4$, then filtered. The solvent was removed under vacuum producing a colorless oil which solidified as an off-white powder from ethanol/ether solution overnight at –10 °C. Yield 72%, m.p. = 145–148 °C. *Anal.* Calc. for $C_{27}H_{44}N_4O_4$: C, 61.83; H, 9.16; N, 10.68. Found: C, 62.76; H, 8.85; N, 10.53%. Mass spectrum: (488 g mol^{-1}, *m/z*); 489(m + 1$^+$, 4.7); 390(3.2); 376(10.6); 364(18.9); 265(23.3); 252(12.7); 240(15.9); 183(16.7); 167(15.7); 125(98.8); 112(100); 98(89.2); 84(91.2); 70(95.9); 54(61.1). ^{1}H NMR ($CDCl_3$, δ): 1.73(s, 6H); 1.75(s, 6H); 1.82(s, 6H); 1.34(m, 2H); 1.62(p, 4H); 2.05(t, 4H); 3.27(t, 8H); 4.83(s, 4H); 10.76(s, 4H). IR (KCl, cm^{-1}): ν(C=O) 1610, 1580 cm^{-1}.

5,8,23,26-Tetraaza-4,9,22,27-tetramethyltricontane-2,11,20,29-tetraone (octyl-bis(1-bae)) (5)

Compound **5** was prepared using the same method used to prepare **4** except 3.67 g (0.013 m) of octyl bis(1-acac) (**2**) were substituted for **1**. Crystallization from ethanol/ether yielded 5.1 g (74%) of **5** as an off-white powder, m.p. = 157–160 °C. *Anal.* Calc. for $C_{30}H_{50}N_4O_4$: C, 65.69; H, 9.49; N, 10.22. Found: C, 65.98; H, 9.66; N, 9.29%. Mass spectrum (530 g mol^{-1}, *m/z*): 531(m + 1^{1+}, 1.4); 432(1.0); 418(2.3); 406(4.2); 307(4.2); 57(6.4). ^{1}H NMR ($CDCl_3$, δ): 1.09(m, 8H); 1.36(p, 4H); 2.00(t, 4H); 1.72(s, 12H); 1.78(s, 6H); 3.24(t, 8H); 4.80(s, 4H); 10.72(s, 4H). IR (KCl, cm^{-1}): ν(C=O) 1610, 1580 cm^{-1}.

Synthesis of Metal Complexes (Fig. 2)

Pentyl-bis(Ni(1-(bae))) (6)

A 0.552 g (1.13 mmol) amount of 4 was dissolved in 20 ml warm methanol under a dry nitrogen atmosphere. To the stirred solution was added 0.600 g (2.80 mmol) of nickel(II) acetate dihydrate previously dissolved in 25 ml of hot methanol producing a dark red–brown solution. The reaction was stirred at 55–60 °C for 2 h at which time the solvent was removed *in vacuo*, yielding a red–brown oil. Excess

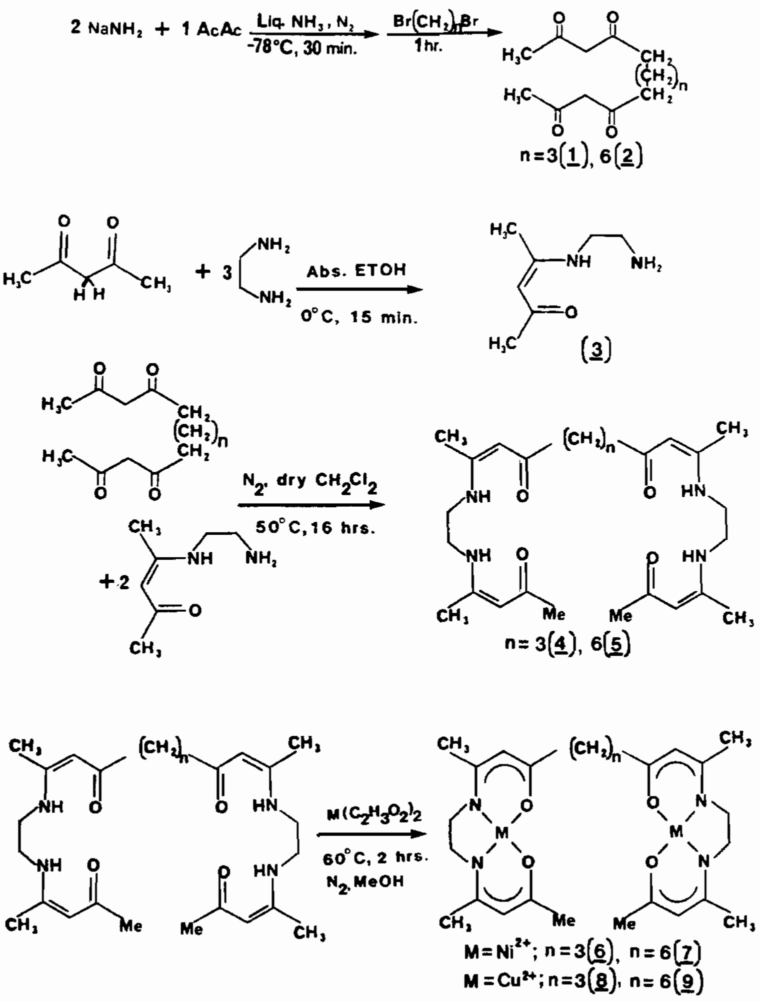


Fig. 2. Procedures used to prepare ligands and their metal complexes.

nickel(II) acetate was removed by dissolving the oil in dichloromethane and filtering. The filtrate was dried with $MgSO_4$ and the solvent removed on a rotary evaporator. Solidification of the resulting oil was achieved by adding 1–2 ml of anhydrous diethyl ether and placing the mixture *in vacuo* for several hours. Compound **6** was isolated as a red–brown, amorphous solid in 81% yield (0.552 g), m.p. = 119–122 °C. *Anal.* Calc. for $Ni_2C_{27}H_{40}N_4O_4$: Ni, 19.52; C, 53.85; H, 6.65; N, 9.31. Found: Ni, 19.11; C, 54.73; H, 7.04; N, 8.91%. ^1H NMR ($CDCl_3$, δ): 1.24(m, 2H); 1.64(p, 4H); 1.76(s, 6H); 1.77(s, 6H); 1.81(s, 6H); 2.05(t, 4H); 3.05(t, 8H); 4.84(s, 4H). IR (KCl, cm^{-1}): ν(C=O) 1575, ν(C=N) 1510, ν(M–N) 482 cm^{-1}. UV–Vis (CH_2Cl_2: λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 567(113).

Octyl-bis(Ni(1-bae)) (7)

The same method used to prepare **6** was used to prepare **7** with 0.600 g (1.13 mmol) of **5** being substituted for **4**. Solidification from ether *in vacuo* yielded 0.554 g (76%) of **7**; m.p. = 126–128 °C. *Anal.* Calc. for $Ni_2C_{30}H_{46}N_4O_4$: Ni, 18.25; C, 55.95; H, 7.15; N, 8.70. Found: Ni, 18.53; C, 56.40; H, 7.52; N, 8.25. ^1H NMR ($CDCl_3$, δ): 1.16(m, 8H); 1.40(p, 4H); 1.77(s, 6H); 1.79(s, 6H); 1.81(s, 6H); 2.00(t, 4H); 2.99(t, 8H); 4.82(s, 4H). IR (KCl, cm^{-1}): ν(C=O) 1575, ν(C–N) 1510, ν(M–N) 482 cm^{-1}. UV–Vis (CH_2Cl_2), λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 567-(112).

Pentyl-bis(Cu(1-bae)) (8)

The same method used to prepare **6** was used to prepare **8** except 0.617 g (2.8 mmol) of copper acetate dihydrate was used in place of the nickel acetate. Workup identical to that of the nickel complexes yielded 0.484 g (70%) of purple powder which analyzed as **8**. Loss of solvent decomposition 76–78 °C, m.p. 118–120 °C. *Anal.* Calc. for $Cu_2C_{27}H_{40}N_4O_4$: Cu, 20.65; C, 53.03; H, 6.55; N, 9.17. Found: Cu, 20.20; C, 53.95; H, 6.93; N, 8.69%. IR (KCl, cm^{-1}): ν(C–O) 1580, ν(C–N) 1510,

ν(M–N) 459 cm^{-1}. UV–Vis (CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 547(365), and 655sh(198).

Octyl-bis(Cu(1-(bae))) (9)

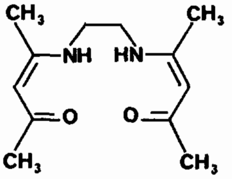
0.600 g (1.13 mmol) of 5 was reacted with 0.617 g (2.8 mmol) of copper acetate following the procedure for the other binuclear metal complexes yielding 0.460 g (62%) of 9, m.p. 120–122 °C. *Anal.* Calc. for $Cu_2C_{30}H_{46}N_4O_4$: Cu, 19.35; C, 55.13; H, 7.04; N, 8.57. Found: Cu, 19.31; C, 54.72; H, 7.17; N, 8.50%. IR (KCl, cm^{-1}): ν(C–O) 1580, ν(C–N) 1510, ν(M–N) 459 cm^{-1}. UV–Vis (CH_2Cl_2; λ_{max}, nm (ϵ, (M^{-1} cm^{-1}): 547(365), and 655sh(198).

Results and Discussion

Ligand Synthesis and Characterization

Two binucleating ligands, pentyl-bis(1-(bae)) (4) and octyl-bis(1-(bae)) (5), including their binuclear Ni(II) (6 and 7) and Cu(II) (8 and 9) complexes, have been prepared [22] following the procedure outlined in Fig. 2. Starting compounds 1, 2, and 3 were prepared from slightly modified procedures published previously by others [21, 23]. High yields of the binucleating Schiff base complexes are obtained from the condensation of two equivalents of 3 with one equivalent of 1 or 2 in dichloromethane, followed by crystallization from ethanol/ether solutions.

The binucleating ligands and their metal complexes have been characterized by IR, mass spectrometry, and ^{1}H and ^{13}C NMR spectroscopy. The diffuse reflectance infrared spectra of 4 and 5 show two strong absorptions at 1610 and 1580 cm^{-1}. These bands are assigned to the ν(C=O) stretch of the ketoamine form of the molecule. A broad band at 1608 cm^{-1} has been reported for the ketoamine form of bis(acetylacetone)ethylenediamine [23a] (I). In addition, a broad absorption at 3160 cm^{-1} can be assigned to the hydrogen bonded amine ν(N–H) stretch of the molecule. The mass spectra of compounds 4 and 5 show mass ions at 488 and 530 mass units and fragmentation patterns consistent with the proposed structures.



bae

The 300 Mz ^{1}H NMR spectrum of pentyl bis(1-(bae)) (4) is shown in Fig. 3. The spectrum of 5 is very similar to the spectrum of 4 and relevant spectral data for both molecules and their Ni(II) complexes are listed in Table 1. Three distinct singlets are observed for 4 at 1.73, 1.75 and 1.82 ppm which are assigned to the three inequivalent sets of methyl protons of the α-substituted bae units. The lack of symmetry within the bae rings arises from the presence of a polymethylene bridge attached to an α position of each chelate unit. Three sets of resonances are observed for the five bridging methylene protons. The triplet at 2.05 ppm is assigned to the two methylenes attached directly to the carbonyl carbon atoms. The pentet at 1.62 ppm is assigned to the methylene protons one carbon

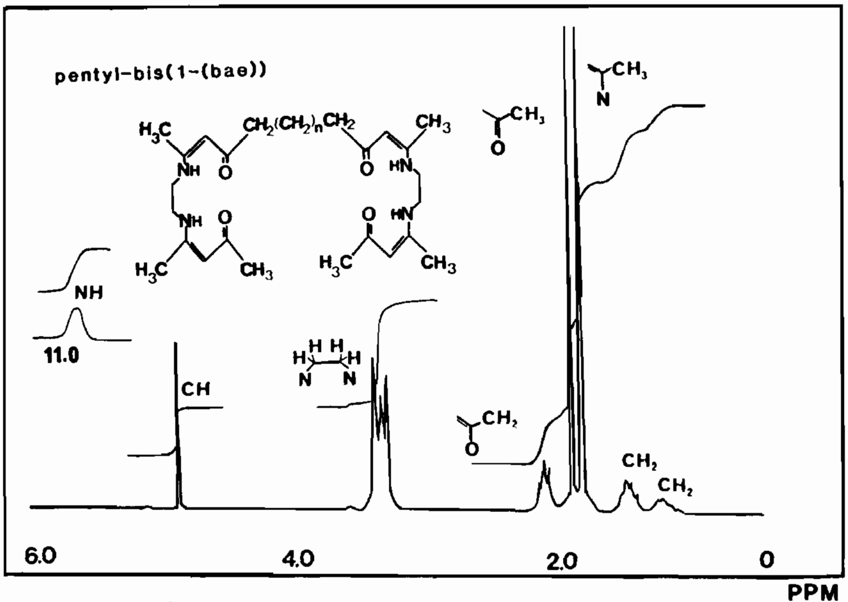
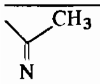
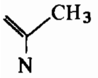
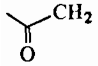


Fig. 3. 300 MHz ^{1}H NMR spectrum of pentyl bis(1-(bae)) in $CDCl_3$.

TABLE 1. 300 MHz ^{1}H NMR Chemical Shifts[a] (ppm) for Compounds **4**, **5**, **6** and **7**

Proton	Chemical shift (ppm) (TMS)			
	4	5	6	7
	1.82s	1.78s	1.81s	1.81s
	1.73s 1.75s	1.72s	1.76s 1.77s	1.77s 1.79s
CH	4.83s	4.80s	4.84s	4.82s
	3.27t	3.24t	3.05t	2.99t
NH	10.76s	10.72s	not present	not present
	2.05t	2.00t	2.05t	2.00t
CH_2	1.62p	1.36p	1.64p	1.40p
CH_2	1.34m	1.09m	1.24m	1.16m

[a] Spectra recorded in $CDCl_3$ relative to TMS as an internal standard (s = singlet, t = triplet, m = multiplet).

removed from the carbonyl carbon atoms, and the central methylene protons of the bridge are observed as a multiplet at 1.09 ppm. The methylene protons of the diaminoethane rings appear as a triplet at 3.27 ppm while the vinylic CH protons are observed as a broad singlet at 4.83 ppm. The relative integration of the proton spectrum of **4** and **5** conforms with the proposed structures in Fig. 1. Finally, a NH resonance is observed as a singlet at 10.76 ppm. This resonance disappears upon addition of D_2O to the NMR solution.

Figure 4 shows the ^{13}C and ^{13}C-APT spectra of pentyl bis(1-(bae)) while a complete list of ^{13}C chemical shift data and assignments for compounds **4**–**7** appears in Table 2. Twelve resonances are observed in the ^{13}C spectrum of **4**, consistent with the proposed structure. Three inequivalent methyl carbon resonances are observed at 18.30, 18.32 and 28.40 ppm, and two inequivalent vinylic carbon resonances are observed at 95.50 and 95.95 ppm. In addition, two inequivalent carbonyl carbon resonances at 195.18 and 198.48 ppm support the unsymmetric structure proposed for this compound. Single carbon resonances are observed for the diaminoethane carbon atoms and the enamine carbon atoms at 43.16 and 162.80 ppm, respectively. Finally, the three remaining carbon resonances in the spectrum are assigned to the bridging methylene carbon atoms. Compound **5** has thirteen inequivalent carbon atoms and the position of these resonances and their assignments are listed in Table 2.

Definitive assignment of all of the carbon atoms in **4** and **5** has been accomplished with the use of ^{13}C-APT NMR. Figure 4 shows the ^{13}C-APT spec-

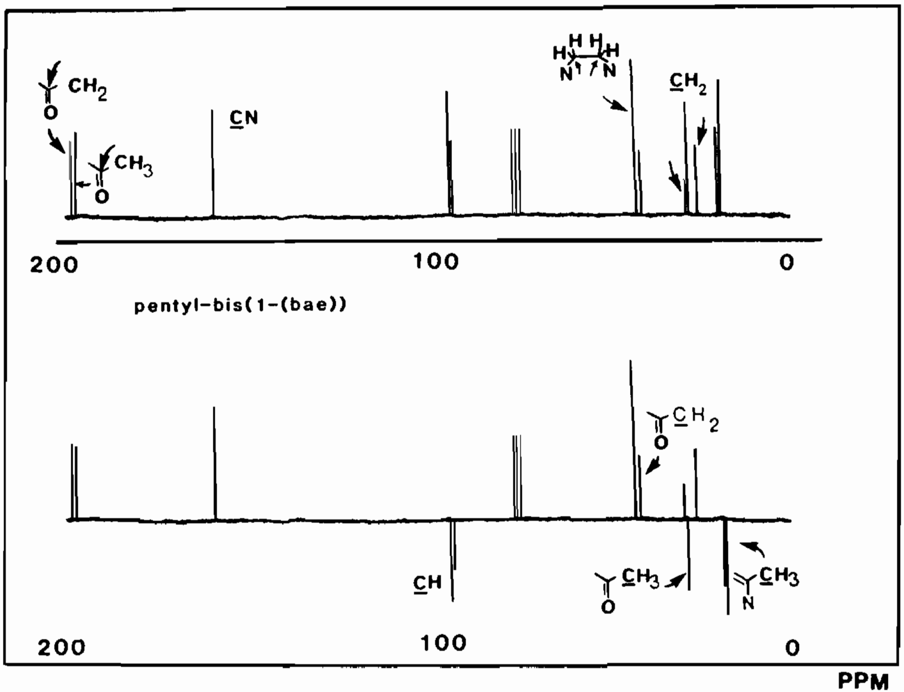
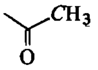
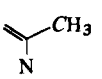
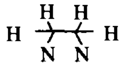
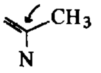
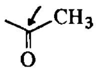
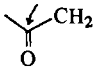
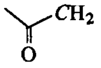


Fig. 4. 22.5 mHz ^{13}C and ^{13}C-APT spectra of pentyl bis(1-(bae)) in $CDCl_3$.

TABLE 2. 22.5 MHz ^{13}C NMR Chemical Shifts^{a} (ppm) for Compounds 4, 5, 6 and 7

Carbon	Chemical shift (ppm) (TMS)			
	4	5	6	7
	28.40	28.40	27.40	27.40
	18.30 18.32	18.32 18.34	21.00 21.12	21.00 21.11
CH	95.50 95.95	95.48 96.00	98.26 99.33	98.26 99.35
	43.16	43.16	38.11	38.11
	162.80	162.80	164.34	164.34
	195.18	195.20	176.53	176.53
	198.48	198.60	180.13	180.13
	41.52	41.60	29.40	29.40
CH_2	28.80	29.02	29.18	29.20
CH_2	26.60	29.00	26.70	29.09
CH_2	not present	25.80	not present	24.23

^{a}Spectra recorded in $CDCl_3$ relative to TMS as an internal standard.

trum of 4. As expected, carbon atoms bonded to an odd number of hydrogen atoms are inverted while carbon atoms having an even number of protons remain upright. The ^{13}C-APT data for both compounds is consistent with their proposed structures.

Metal Complexes

Nickel(II) complexes

Ni(II) complexes of 4 and 5 are prepared by reacting the ligands with a slight excess of two equivalents of nickel(II) acetate dihydrate in warm methanol. Compounds 6 and 7 are isolated as red–brown powders and are soluble in most organic solvents. Elemental analyses of 6 and 7 are in good agreement with theoretical values based on the proposed structures in Fig. 1. The IR spectra of 6 and 7 show two strong bands at 1575 and 1510 cm^{-1} attributed to the $\nu(\mathrm{C}\overset{..}{-}\mathrm{O})$ and $\nu(\mathrm{C}\overset{..}{-}\mathrm{N})$ stretching modes of the Schiff bases. Similar spectral properties have been reported for other Ni(II) Schiff base complexes [23]. The electronic spectrum of the nickel complexes, shown in Fig. 5, displays a broad band at 567 nm which is characteristic of square-planar, d^{8}, nickel(II) complexes [24].

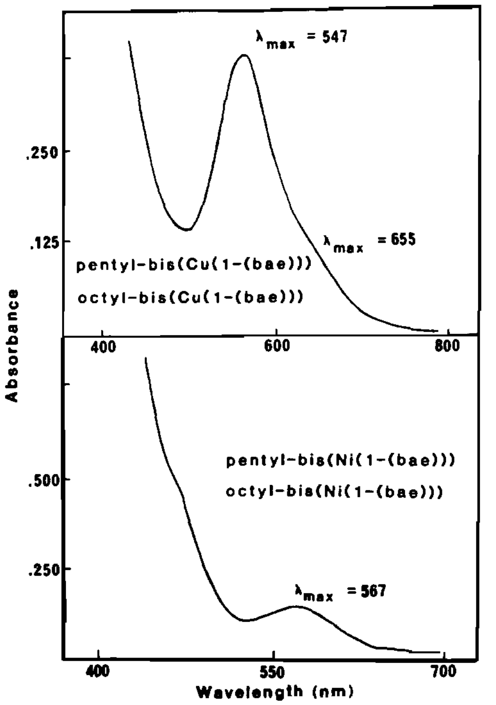


Fig. 5. Electronic spectra of compounds 6, 7, 8 and 9 in dichloromethane. The concentration of nickel complexes is 1.3 × 10^{-3} M. The concentration of copper complexes is 1.0 × 10^{-3} M.

The nickel(II) complexes are diamagnetic and therefore have been characterized by ^{1}H and ^{13}C NMR spectroscopies. Tables 1 and 2 contain ^{1}H and ^{13}C data and their respective assignments. The most notable feature in the proton spectrum is the absence of the NH resonance at 10.7 ppm indicative of Ni(II) ion coordination. Both the ^{1}H and ^{13}C spectra of the Ni complexes are very similar to the spectra of the free ligands indicating minor structural changes have occured within the molecules upon coordination of the metal ion. Similar ^{1}H and ^{13}C chemical shifts have been reported for Ni(bae) [23a], supporting our assignments in Tables 1 and 2.

Copper(II) complexes

Cu(II) complexes of 4 and 5 are prepared by reacting the appropriate ligands with copper(II) acetate monohydrate in warm methanol. The complexes are isolated as purple solids in good yields and are soluble in most organic solvents. Elemental analyses of 8 and 9 are consistent with their proposed structures. The copper complexes show $\nu(\mathrm{C}\overset{..}{-}\mathrm{O})$ and

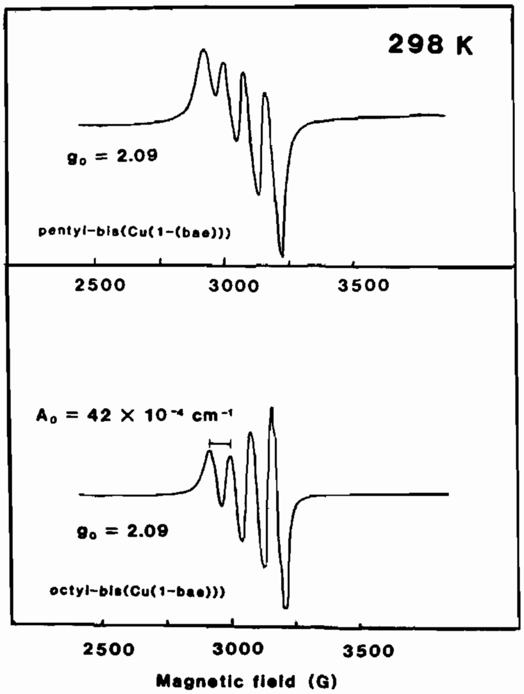


Fig. 6. EPR spectra of compounds 8 and 9 at a concentration of 4.0 X 10^{-3} M in toluene at 298 K.

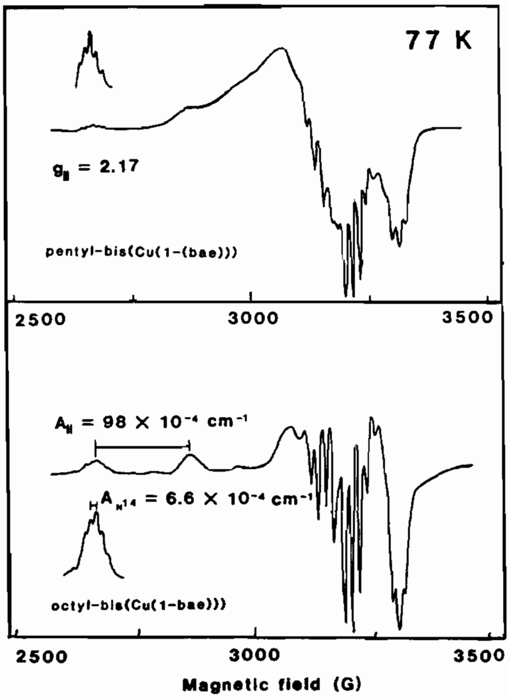


Fig. 7. Frozen toluene solution EPR spectra of compounds 8 and 9 at 77 K.

ν(C$\overset{..}{-}$N) IR stretches at 1575 and 1510 cm^{-1}, respectively. Comparable results have been reported for Cu(bae) [25]. Figure 5 shows the electronic spectra of the copper complexes. Each complex has an absorption band centered at 547 nm with a shoulder at 655 nm. Similar results have been reported for the spectrum of Cu(bae) [25]. The room temperature magnetic moments of 8 and 9 are μ_{eff} = 1.95 BM/Cu, consistent with other square-planar d^9 complexes [26].

EPR Spectra of Copper(II) Complexes

The room temperature EPR spectra of 8 and 9 are illustrated in Fig. 6. Identical spectra are obtained for both compounds in either dichloromethane or toluene solutions. The results (g_0 = 2.09 and $|A_0|$ = 42 X 10^{-4} cm^{-1}) are typical of isotropic spectra observed for mononuclear Cu(II) complexes such as Cu(bae) (g_0 = 2.09 and $|A_0|$ = 41.8 X 10^{-4} cm^{-1}); suggesting that the two metal ions are magnetically isolated from each other. Double integration of the room temperature EPR spectra of both pentyl-bis(Cu(1-bae)) and octyl-bis(Cu(1-bae)) reproducibly give nearly twice the integrated area compared to stoichiometric quantities of mononuclear standards such as Cu(bae) and $CuSO_4$. The long aliphatic chains presumably provide enough spatial separation between metal ions precluding spin–spin exchange coupling.

The frozen-solution spectra of 8 and 9 at 77 K are shown in Fig. 7. The spectra are typical of tetragonal mononuclear Cu(II) complexes ($g_\parallel$ = 2.17, $|A_\parallel|$ = 98 X 10^{-4} cm^{-1}) [27]. Each $g_\parallel$ line in the frozen-solution spectrum of 9 is split into five lines due to the coupling of the metal d electron with two nitrogen nuclei. The 77 K spectrum of 8 is less clearly resolved. The nitrogen superhyperfine coupling constants in both spectra are 6.6 X 10^{-4} cm^{-1}. No ΔM_s = 2 transition at half-field was observed for either complex at 77 K. It is evident from EPR spectra of 8 and 9 that the copper(II) ions remain magnetically non-coupled at both room temperature and liquid nitrogen temperatures.

In a previous study, we observed similar magnetic behavior for a *m*-xylyl bridged binuclear Schiff base Cu(II) complex [18]. The room temperature and frozen-solution spectral parameters of *m*-xyl-bis-(Cu(3-(bae))) are g_0 = 2.09, $|A_0|$ = 42 X 10^{-4} cm^{-1}, and $g_\parallel$ = 2.17 and $A_\parallel$ = 98 X 10^{-4} cm^{-1}, respectively. Kida and coworkers have observed varied magnetic behavior for several aliphatic bridged bis-macrocyclic copper(II) complexes [28]. Complexes containing short chain lengths (2–3 methylene carbon atom bridges) show the presence of spin exchange coupling between copper centers. Longer chain-length bis-macrocyclic complexes produce spectral features characteristic of magnetically non-coupled monomeric copper(II) complexes. The synthesis of binuclear Schiff base complexes containing chain lengths shorter than those in 8 and 9 is in progress and the magnetic properties of these complexes will be the subject of future studies.

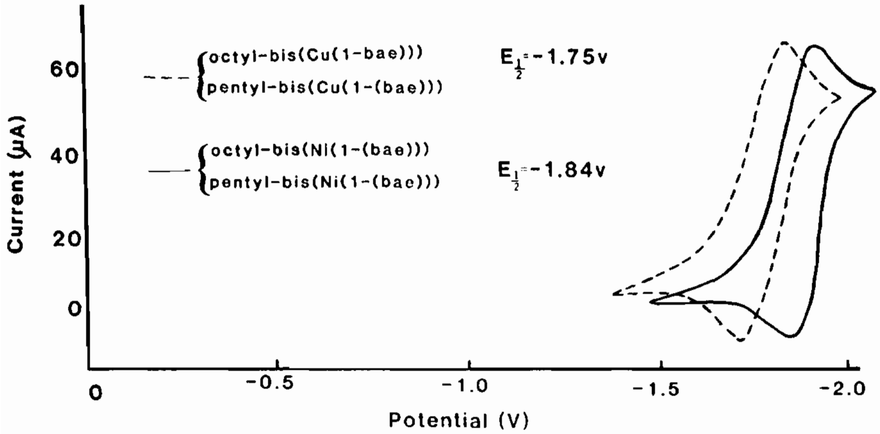


Fig. 8. Cyclic voltammograms of 6 (5.1×10^{-3} M), 7 (5.0×10^{-3} M), 8 (5.1×10^{-3} M), and 9 (5.2×10^{-3} M) in DMF and 0.1 M TBAP at a glassy-carbon electrode. All $E_{1/2}$ values are referenced to a Ag/AgCl electrode.

Electrochemistry

Cyclic voltammograms of compounds **6**–**9** have been recorded in DMF solutions (containing 0.1 M tetra-n-butylammonium perchlorate) at a glassy carbon electrode (Fig. 8). Only one quasi-reversible wave is observed for each compound between the potential limits of 0 to −2.5 V *versus* Ag/AgCl. The nickel(II) complexes display $E_{1/2}$ values of −1.84 V *versus* a Ag/Ag reference electrode while the copper(II) complexes display $E_{1/2}$ values of −1.75 V. The peak-to-peak separation of the anodic and cathodic waves average about 120 mV for all four complexes and do not vary significantly with scan rates between 10 and 100 mV/s. The anodic and cathodic peak currents vary linearly with the square-root of the scan rate within the scan rate range mentioned above. Beyond 100 mV/s scan rates the ratio of peak currents deviates significantly from unity. The large ΔEp is due to the differences in the E_1 and E_2 potentials for two reversible redox processes. Coulometric reduction of the complex yields 1.9 Faradays of current per mole of complex confirming that the redox process proceeds via two monoelectronic steps at nearly the same potential.

Theory for multielectron transfer processes at stationary electrode surfaces using cyclic voltammetry has been developed [29]. A peak-to-peak separation between reduced and oxidized species of 42 mV is predicted for two rapid simultaneous one-electron reduction steps [9, 29]. The larger peak-to-peak separation observed for compounds **6**–**9** do not conform to the theory for a strictly reversible process and suggest that the redox behavior is proceeding in two-successive monoelectronic steps at potentials that are similar but not identical. Evidently the broadness of the voltammograms and quasi-reversible nature of the redox process precludes detection of any splitting of the waves.

Further support for closely spaced sequential redox steps comes from a comparison of the cyclic voltammetric properties of compounds **6**–**9** and their monomeric analogs, Cu(bae) and Ni(bae). In general, the binuclear complexes produce twice the current observed for equimolar concentrations of the monomeric species. Apparently the long chain lengths of the bridges provide enough distance between metal centers to effectively insulate them electronically on the electrochemical time scale. These results are in agreement with the magnetic properties of the bis-macrocyclic complexes discussed earlier.

Electrochemical and magnetic behavior similar to compounds **8** and **9** have been reported for binuclear copper(II) cryptate [5b, 16], and binuclear copper(II) complexes of the planar polyketonate [8] 1-phenyl-1,3,5-hexanetriketonate [8]. However, in the latter two complexes the redox reactions are occurring via two sequential one-electron steps at the same electrochemical potential. Further studies are in progress to determine the diffusion coefficients and rate constants for the reduction processes of **6**–**9** and to establish the origin of their large peak-to-peak separations.

Conclusions

Two new binucleating Schiff base macrocycles, **4** and **5**, have been prepared and characterized. Both ligands form stable Cu(II) and Ni(II) complexes. The electronic and magnetic properties of compounds are characteristic of square-planar complexes. Unlike the γ-branched [18] analogs that display irreversible electrochemical behavior compounds **6**–**9** undergo two quasi-reversible monoelectronic reduction processes at nearly the same potential. No magnetic exchange between Cu(II) ions in solution was detected at either room or liquid nitrogen temperatures indicating that the metal centers are magnetically isolated. Thus the binuclear Schiff base macrocycles may be considered as potential two-electron 'receptor units' [5b, 16] which could potentially accept two electrons from a single bridged substrate molecule. Compounds such as these could ultimately function as electron transfer catalysts for reactions requiring multiple electron-transfer steps. They may also help elucidate how multielectron transfer metalloproteins function and control their unique redox behavior.

Supplementary Material

Complete mass spectra of compounds are available upon request from the authors.

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