Pergamon

PII: S0277-5387(96)00596–7

Polyhedron Vol. 16, No. 15, pp. 2659–2665, 1997

0277–5387/97 $17.00+0.00

Synthesis, magnetism and electrochemistry of tetranuclear nickel(II) and copper(II) complexes of an unsymmetrical bis-pentadentate Schiff-base ligand

Paul E. Kruger,[a] Boujemaa Moubaraki[b] and Keith S. Murray[b]*

[a]Department of Chemistry, Trinity College, Dublin 2, Ireland

[b]Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia

(Received 30 August 1996; accepted 4 December 1996)

Abstract—A new unsymmetrical tetranucleating ligand, H_6L, containing salicylideneimine and acetylacetoneimine end groups attached to a propan-2-ol backbone, has been synthesized. The ligand results from the Schiff-base condensation of 1-(1-methyl-3-oxobut-1-enylamino)-3-(amino)propan-2-ol and the dialdehyde, 5,5′-methylene-bis-salicylaldehyde (2 : 1). Tetranuclear nickel(II) and copper(II) complexes of this ligand, of the type $[M_4L(X)_2]$, containing either μ-pyrazolate (X = pz) or μ-3,5-dimethylpyrazolate (X = Me_2pz) exogenous bridges in conjunction with μ-alkoxo endogenous bridges, have been synthesized. Magnetic susceptibility studies on powdered samples of $[Cu_4L(pz)_2]$ (**3**) show medium-strength antiferromagnetic coupling ($J_{12} = -108$ cm^{-1}) within each half of the tetranuclear complex together with a weaker antiferromagnetic coupling ($J_{\text{intermol.}} = -55$ cm^{-1}) between the molecules. Cyclic (CV), Osteryoung square wave (OSWV) and Normal pulse (NPV) voltammetric studies on dimethylformamide solutions of $[Ni_4L(Me_2pz)_2]$ (**2**) revealed waves attributable to two sequential one-electron metal centred reduction processes (×2) to yield $[Ni_4L(Me_2pz)_2]^{2-}$ and $[Ni_4L(Me_2pz)_2]^{4-}$. © 1997 Elsevier Science Ltd

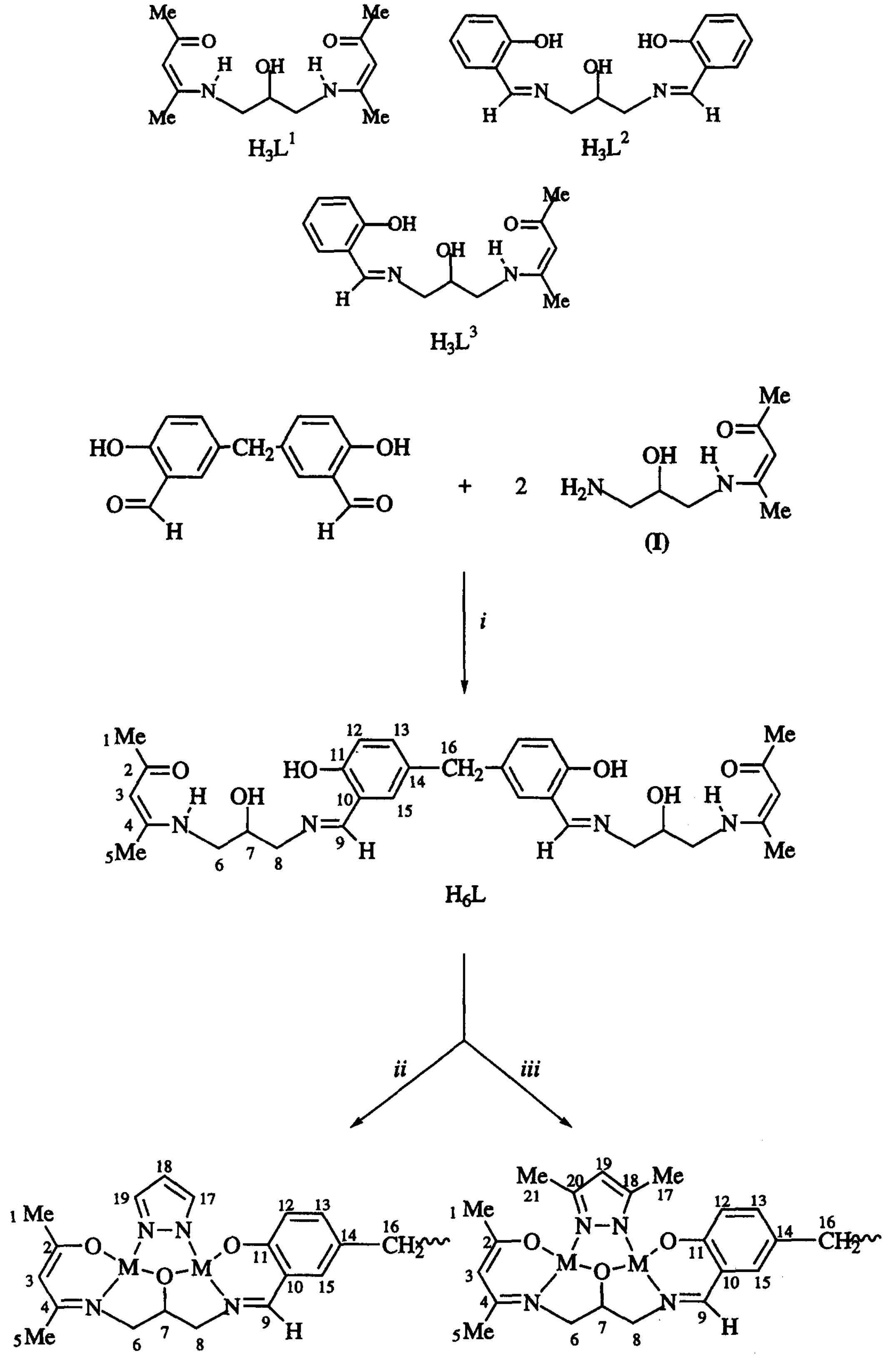
Keywords: nickel(II); copper(II); tetranuclear; unsymmetrical; Schiff-base; magnetism.

Polynucleating ligands possessing the ability to coordinate two or more transition metals within close proximity to each other have attracted considerable interest within recent years [1]. In addition to an intrinsic chemical and structural interest in the development of novel multi-metallic systems incorporating varied ligand types, inspiration for this research is drawn from, amongst others, biomimetic [2], reactivity/catalytic [3] and magneto-structural [4] quarters. Whilst the field of binucleating ligands has developed considerably, tetranucleating ligands have been less well explored. In this regard, a relatively fertile area of research has utilized macrocyclic ligands, formed *via* the cyclo-condensation of various dialdehydes with several diamines, to yield tetranuclear Cu^{II}, $Mn^{II/III}$, $Co^{II/III}$, Ni^{II} and Zn^{II} species [1,5]. These ligand systems have also been found to form higher order aggregates incorporating additional metal centres within their ligand cavities [6]. In an analogous fashion, Thompson *et al.* [7] have employed a non-macrocyclic pyridylamino-phthalazine ligand to form a series of tetranuclear Cu^{II} complexes. To date, however, examples of the above systems have retained a certain degree of symmetry, with respect to the metal centres, and thus there is somewhat of a dearth of tetranucleating ligands capable of conferring an unsymmetrical nature upon any subsequent complexes formed. In this respect, we recently reported the preparation of the unsymmetrical ligand, H_3L^3, and its binuclear Cu^{II} and Ni^{II} complexes [8].

The synthesis of H_3L^3 involved the use of the amine intermediate, (**I**). Utilizing this intermediate in the present study, we have prepared the new tetranucleating bis-pentadentate ligand H_6L, through the Schiff-base condensation of (**I**) with the dialdehyde 5,5′-methylene-bis-salicylaldehyde (Scheme 1). Herein, we also report the preparation of tetranuclear

---

* Author to whom correspondence should be addressed.



(1) M = Ni
(3) M = Cu

(2) M = Ni
(4) M = Cu

Scheme 1. Numbering scheme refers to ^{13}C NMR assignments. (i) MeOH/THF solvent (1 : 1); (ii) $M(ClO_4)_2$ (M = Cu^{II} or Ni^{II}), pyrazole, KOH, MeOH solvent; (iii) $M(ClO_4)_2$ (M = Cu^{II} or Ni^{II}), dimethylpyrazole, KOH, MeOH solvent.

Cu^{II} and Ni^{II} complexes of this novel ligand and make comparisons between these and the binuclear complexes formed by the related unsymmetrical [8] ligand, H_3L^3, and the symmetrical analogues [9,10] incorporating H_3L^1 and H_3L^2.

EXPERIMENTAL

CAUTION! Although no problems were encountered in the present study, perchlorate salts are potentially explosive and should only be handled in small quantities.

Materials

All chemicals and solvents used were of reagent grade. Solvents and chemicals used for physical and electrochemical measurements were of spectroscopic grade. $Cu(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$ and pyrazole, 3,5-di-methylpyrazole and 1,3-diamino-propan-2-ol were obtained with Aldrich Chemical Co. 2,4-Pentanedione was obtained from Hopkin and Williams Ltd. Salicylaldehyde was obtained from Riedel-de Haën.

Preparation of 5,5′-methylene-bis-salicylaldehyde

A slight modification to the procedure of Marvel and Tarköy [11] was used to prepare the dialdehyde. A mixture consisting of concentrated sulfuric acid (0.25 cm^3) and glacial acetic acid (1.25 cm^3) was slowly added, at a temperature of 90–95°C, to a stirred anaerobic (N_2) glacial acetic acid solution (50 cm^3), containing salicylaldehyde (40 g, 0.327 mol) and trioxane (3.5 g, 3.85 mmol). The mixture was maintained under nitrogen at this temperature with stirring for a further 22 h. The resulting reaction mixture was then poured into 3 l of ice-water, to precipitate a pinkish coloured solid, and allowed to stand overnight. The solid was collected by filtration and thoroughly washed with diethylether (100 cm^3), to remove excess salicylaldehyde, and petroleum spirit (b.p. 40–60°C) and air dried. Recrystallization from acetone retrieved a cream coloured crystalline solid. m.p. 136–138°C (lit. 140–141°C) [11]. Infrared spectrum (Nujol): 1656vs, 1620sh, 1589s, 1480vs, 1323m, 1274s, 1235m, 1212m, 1196m, 1147m, 917w, 895w, 875w, 844w, 828m, 810w, 768s, 746vs, 719m, 677s and 617m cm^{-1}. ^1H NMR spectrum (d_6-acetone, 200 MHz): 10.86 (bs, 2H, ex, Ar—OH); 9.98 (s, 2H, CHO); 7.64 (s, 2H, phenyl); 7.48 (d, 2H, phenyl); 6.92 (d, 2H, phenyl) and 4.01 (s, 2H, CH_2) ppm. ^{13}C NMR spectrum (d_6-acetone, 50 MHz): 197.8(C1); 160.7(C7); 138.4(C3); 134.2(C5); 133.7(C2); 121.7(C4); 118.2(C6) and 39.8(C8) ppm. N.B. This numbering scheme is different to that of H_6L. C1 is CHO, C7 is COH, C8 is CH_2, C2–C6 aromatic C.

Preparation of tetranucleating ligand H_6L

A chloroform solution (50 cm^3) containing freshly distilled 2,4-pentanedione (5.01 g, 0.05 mol) was added dropwise to a vigorously stirred chloroform solution of 1,3-diaminopropan-2-ol (4.44 g, 0.05 mol) over a period of some 30 min. After the addition was complete the solution was allowed to stand at ambient temperature for 8 h, after which time the solvent was removed under reduced pressure to retrieve a viscous yellow oil or a milky yellow slurry [8]. This intermediate, (**I**), was then used directly in the subsequent step. The residue was dissolved in a methanol/tetrahydrofuran (1 : 1) solvent mix, warmed slightly and to this was added, with stirring, a tetrahydrofuran solution of 5,5′-methylene-bis-salicylaldehyde. Reduction of solvent volume and addition of petroleum spirit (b.p. 40–60°C), followed by storage within a refrigerator, yielded the ligand as a golden-yellow coloured solid. M.p. 67–70°C. Found: C, 65.7; H, 7.0; N, 9.8. $C_{31}H_{40}N_4O_6$ requires: C, 65.9; H, 7.1; N, 9.9%. Ultraviolet-visible spectrum (acetone): λ/nm (ε; $dm^3\ mol^{-1}\ cm^{-1}$) 328 (12440). Infrared spectrum (Nujol, cm^{-1}): 3220mbr, 1638vs, 1605vs, 1556s, 1522m, 1492s, 1440sh, 1340sh, 1298m, 1274m, 1226wsh, 1159w, 1102w, 1021w, 983w, 938w, 823m, 784m and 750m. ^1H NMR spectrum (d_6-DMSO, 200 MHz): 13.21 (brs, 2H, ex. Ar—OH); 10.77(brm, 2H, ex, CNH); 8.45(s, 2H, imine), 7.27(s, 2H, phenyl); 7.18(d, 2H, phenyl), 6.81(d, 2H, phenyl); 5.34(brs, 2H, ex, C—OH); 4.94(s, 2H, methine); 3.83–3.10(m, 12H, methine, methylene), 1.90(s, 6H, CH_3); 1.86(s, 6H, CH_3) ppm. ^{13}C NMR spectrum (d_6-DMSO, 50 MHz): 192.8(C2), 167.0(C9), 162.9(C4), 158.9(C11), 132.7(C13), 131.5(C14), 131.4(C12), 118.5(C10), 116.5(C15), 94.9(C3), 69.2(C7), 62.5(C8), 46.5(C6), 46.0(C16), 28.6(C1) and 18.7(C5) ppm. Mass spectrum *m*/*z*: 276($C_{15}H_{19}N_2O_3^+$, 8%), 142($C_7H_{12}NO_2^+$, 100), 112 ($C_6H_{10}NO^+$, 100), 98(90), 84(80).

Preparation of tetranuclear $[M_4L(X)_2]$ complexes of H_6L [X = pz, Me_2pz; $M = Ni^{II}$ and Cu^{II}]

A methanolic solution of KOH (8×10^{-3} mol) was added, with vigorous stirring, to a methanol/tetrahydrofuran (1 : 1) solvent mixture containing H_6L (1×10^{-3} mol), pyrazole (2×10^{-3} mol) and metal perchlorate salt (4×10^{-3} mol). This resulted in the formation of either a red-brown (Ni), violet (Cu, pz) or green (Cu, Me_2pz) coloured slurry. After 20 min, the mixture was filtered to remove the solids and allowed to dry. Purification was achieved by Soxhlet extraction over a period of several days using a chloroform/dichloromethane solvent mix. Attempts to obtain single crystals were thwarted by the complexes' lower solubility in appropriate crystallizing solvents. Low solubility also impinged upon the NMR spectroscopy and resultant spectra contained high noise to signal ratios. In each case the methylene carbon (C16) may be obscured by the solvent (DMSO) resonant peaks (δ 38–41 ppm) and was not observed.

$[Ni_4L(pz)_2]$ (**1**) Found: C, 48.0; H, 4.5; N, 11.7. $C_{37}H_{40}N_8O_6Ni_4$ requires: C, 47.9; H, 4.7; N, 12.1%. Ultraviolet-visible spectrum (DMF): λ/nm (ε; dm^3 mol^{-1} cm^{-1}) 331(14179) 366(10255), 415(4320), 443sh(3368). Infrared spectrum (Nujol, cm^{-1}): 1628s, 1597s, 1535msh, 1509vs, 1316m, 1283m, 1215w, 1183w, 1160w, 1045s, 952w, 830w, 751s and 638m. ^{13}C NMR spectrum (d_6-DMSO, 50 MHz): 174.1(C2), 165.1(C4), 162.3(C9), 161.4(C11), 136.8(C17), 136(C19), 134.3(C13), 132(C12), 127.1(C14), 121(C15), 120.5(C10), 102.8(C18), 99.6(C3), 78.5(C7), 60.5(C8), 54.4(C6), 23.8(C1) and 20.4(C5) ppm.

$Ni_4L(Me_2pz)_2]$ (**2**) Found: C, 52.0; H, 5.6; N, 10.1. $C_{41}H_{48}N_8O_6Ni_4\cdot 2THF$ requires: C, 52.2; H, 5.7; N, 9.9%. Ultraviolet-visible spectrum (DMF): λ/nm (ε; dm^3 mol^{-1} cm^{-1}) 334 (16859), 343(17323), 419(5800). Infrared spectrum (Nujol, cm^{-1}): 1628s, 1594s, 1533msh, 1511vs, 1409s, 1316m, 1299m, 1214w, 1161w, 1137w, 1043m, 952mw, 834m, 764m and 749m. ^{13}C NMR spectrum (d_6-DMSO, 50 MHz): 173.8(C2), 165(C4), 161.8(C9), 161.3(C11), 148.4, 147.7(C18, C20), 134.2(C13), 131.4(C12), 127.6(C14), 120.6(C15), 120.4(C10), 106.7(C19), 99.8(C3), 73.3 (C7), 62.9(C8), 56.8(C6), 23(C1), 20.3(C5) and 12.4, 12.2(C17, C21) ppm.

$[Cu_4L(pz)_2]$ (**3**) Found: C, 44.9; H, 4.6; N, 11.6. $C_{37}H_{40}N_8O_6Cu_4\cdot 2.5H_2O$ requires: C, 44.8; H, 4.5; N, 11.6%. Ultraviolet-visible spectrum (DMF): λ/nm (ε; dm^3 mol^{-1} cm^{-1}) 314 (31116), 370(8465), 568(1283). Infrared spectrum (Nujol, cm^{-1}): 3400–3200wbr, 1637s, 1599s, 1540sh, 1508vs, 1313m, 1280m, 1217w, 1176w, 1157w, 1118w, 1074w, 1041s, 942w, 882w, 827w, 762s, 743m, 721w, 692w and 667w. μ_{eff} 1.60μ_B per Cu at 295 K.

$[Cu_4L(Me_2pz)_2]$ (**4**) Found: C, 49.2; H, 5.0; N, 10.9. $C_{41}H_{48}N_8O_6Cu_4$ requires: C, 49.1; H, 4.8; N, 9.6%. Ultraviolet-visible spectrum (DMF): λ/nm (ε; dm^3 mol^{-1} cm^{-1}) 315(20740), 378(8521), 597(842). Infrared spectrum (Nujol, cm^{-1}): 1637s, 1599s, 1530sh, 1512vs, 1408m, 1339m, 1316m, 1273w, 1216m, 1159m, 1087w, 1039m, 945w, 893w, 826m, 746m, 721m and 668w cm^{-1}. μ_{eff} 1.42μ_B per Cu at 295 K.

Physical methods

Infrared spectra were measured on a Perkin-Elmer 1600 FT-IR instrument with the samples as Nujol mulls between NaCl plates. Abbreviations used: s = strong; m = medium; w = weak; sh = shoulder; br = broad. Chemical analyses; C, H, N, were performed by the Commonwealth Micro-Analytical Services, Melbourne, Australia. Ultraviolet-visible spectra were recorded on a Hitachi 150-20 spectrophotometer using 1 cm quartz cells and solution concentrations of $\sim 10^{-4}$ mol dm^{-3}. Magnetic moments at room temperature were determined using a Faraday balance which incorporated a Newport electromagnet fitted with Faraday-specific pole faces. The instrument was calibrated using $[Ni(en)_3][S_2O_3]$ (en = ethane-1,2-diamine) and $CuSO_4\cdot 5H_2O$. Diamagnetic corrections for ligand susceptibilities were made using Pascal's constants. Variable-temperature magnetic susceptibility measurements (300–4.2 K) were performed on powdered samples at a field strength of 10,000 G (1 T) using a Quantum Design M.P.M.S. Squid magnetometer. The calibration of the instrument was checked regularly against samples of pure palladium and AR $CuSO_4\cdot 5H_2O$. Samples were enclosed in gelatin capsules suspended at the middle of a plastic drinking straw, which was rigidly fixed to the end of the sample rod. Cyclic (CV), Osteryoung square wave (OSWV) and Normal pulse (NPV) voltammetric measurements were carried out using a Bioanalytical System BAS-100 instrument with a three-electrode cell equipped with a platinum or glassy carbon working electrode, a platinum wire auxiliary electrode and a Ag-AgCl (3 mol dm^{-3} NaCl) reference electrode. All measurements were recorded at room temperature in dry, degassed dimethylformamide [$\sim$(1–2)$\times 10^{-3}$ mol dm^{-3}] with tetrabutyl-ammonium perchlorate ($\sim$0.1 mol dm^{-3}) as the supporting electrolyte. Scan rates between 50 and 1000 mV s^{-1} were generally employed, the most common being 100 mV s^{-1}. Proton NMR spectra were measured on Bruker AC200 and AM300 instruments with tetramethylsilane ($SiMe_4$) as internal calibrant. Abbreviations used: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad; ex = exchangeable on D_2O addition. Carbon-13 NMR spectra were recorded with a Bruker AC200 spectrometer using $SiMe_4$ as the internal calibrant and were broad-band decoupled. Mass spectra were recorded on a VG-Micromass 7070F spectrometer.

RESULTS AND DISCUSSION

Synthesis and characterization of H_6L and $[M_4L(X)_2]$ *complexes*

As in the synthesis of the related unsymmetrical pentadentate ligand, H_3L^1, the pivotal intermediate required to make the present bis-pentadentate ligand, H_6L, is the 1:1 Schiff's base condensation product resulting from the reaction of 2,4-pentanedione with 1,3-diaminopropan-2-ol, i.e. acetylacetoneimine-3-aminopropan-2-ol (**I**) (Scheme 1) [8]. The tetranucleating ligand, H_6L, was prepared by reacting intermediate (**I**) with 5,5′-methylene-bis-salicylaldehyde in a 2:1 molar ratio. This required that a mixed solvent, methanol/tetrahydrofuran (1:1), be employed in the second condensation step, as the bis-salicylaldehyde possesses only limited solubility in neat alcohol. The ligand solution was golden-yellow in appearance and yielded a similarly coloured oil on removal of solvent. Dissolution of the oil into tetrahydrofuran, followed

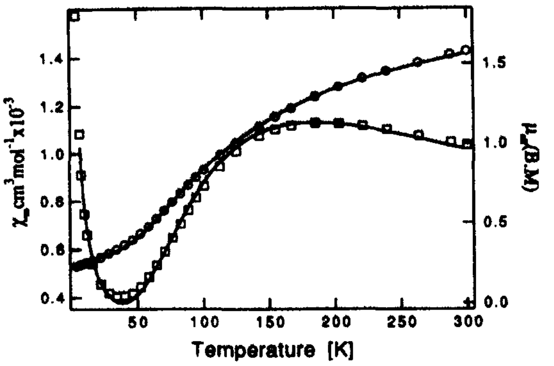


Fig. 1. Temperature dependence of the magnetic susceptibility (□) and magnetic moment (○) for (3). The solid line is that calculated using the parameters in Table 1.

by layering with petroleum spirit (b.p. 40–60°C) and storage within a refrigerator, produced golden coloured microcrystalline samples of H_6L. In addition to elemental analyses, infrared, ^1H and ^{13}C NMR, electronic and mass spectroscopic data are consistent with the desired formulation (Scheme 1). Tetranuclear μ-pyrazolato complexes of the type $[M_4L(X)_2]$ (X = pz, Me_2pz, where pz and Me_2pz are pyrazolate and 3,5-dimethylpyrazolate, respectively) were obtained by treating the metal perchlorate salts (M = Ni or Cu) with H_6L and pyrazole in methanol in the presence of KOH. Recrystallization was achieved *via* Soxhlet extraction ($CH_2Cl_2/CHCl_3$) over a period of several days. The diamagnetic behaviour of the nickel complexes, together with their ^1H and ^{13}C NMR spectra are indicative of planar geometry around each Ni^{II} ion. A *d-d* band at *ca* 570–590 nm in the visible spectra of the violet $[Cu_4L(pz)_2]$ (**3**) and green $[Cu_4L(Me_2pz)_2]$ (**4**) complexes is also indicative of planar geometry around each Cu^{II} ion.

Magnetic exchange in $[Cu_4L(pz)_2]$ (**3**) *and* $[Cu_4L(Me_2pz)_2]$ (**4**)

The effective magnetic moments, per Cu, of 1.60 and 1.42 μ_B for (**3**) and (**4**) respectively, arise from weak to medium strength antiferromagnetic coupling and confirms the anticipated tetranuclear (bis-binuclear) structure of the complexes in which the copper(II) ions are bridged by alkoxo and pyrazalato groups. A variable temperature magnetic susceptibility study was carried out on powdered samples of (**3**) over the temperature range 4.2–300 K. The plot of magnetic susceptibility *vs* temperature for (**3**), as shown in Fig. 1, displays a broad maximum at a temperature of *ca* 190 K indicative of an antiferromagnetically coupled system. A small amount of monomer impurity (*ca* 1.6%) is responsible for the increase in susceptibility at temperatures below 20 K. The corresponding μ_{Cu} values decrease from 1.60 μ_B at 300 K to 0.24 μ_B at 4.2 K. As was found to be the case with the related binuclear complex, $[Cu_2L^3(pz)]$, attempts at fitting the χ *vs* T data in the present system to a simple one-*J* binuclear model was inferior to that obtained when using a two-*J* tetranuclear model [8]. Thus an excellent fit to the data was obtained for the parameter values given in Table 1. As is evident from Table 1, the magnetic behaviour displayed by compound (**3**) is very similar to that of the related unsymmetrical binuclear complex, $[Cu_2L^3(pz)]$, with both the inter- and intra-molecular exchange parameters, *J*, being of comparable magnitude. The intramolecular interaction is, as expected, the dominant exchange pathway, $2J = -216\ cm^{-1}$, and falls within the range of values found for similarly pyrazalato/alkoxo bridged systems [8,9,12].

Electrochemistry of $[Ni_4L(Me_2pz)_2]$ (**2**) *in dimethylformamide solution*

In addition to CV and OSWV measurements, normal pulse voltammetric (NPV) scans were performed upon the tetranuclear complex, $[Ni_4L(Me_2pz)_2]$ (**2**). Insufficient solubility in suitable solvent precluded similar experiments on (**1**), (**3**) and (**4**). Nevertheless, the presence of two primary reduction processes, I and II, are clearly evident for the scans performed upon (**2**) (Table 2). Process I is quasi-reversible with $E_{1/2} = -2.03$ V, $\Delta E_p = 72$ mV and a current ratio $ip^a/ip^c = 0.95$. II has a cathodic peak (*ca* -2.75 V) of comparable current magnitude to that of I, but a

Table 1. Parameters used to fit the magnetic behaviour of the unsymmetrical copper(II) complex (3) and those for related complexes

Compound	μ per Cu (300 K)	g	$2J_1$ (cm^{-1})	$2J_2$[a] (cm^{-1})	% monomer	Reference
$[(Cu_4L)(pz)_2]$ (3)	1.60	1.99	−216	−110	1.6	t.w.
$[(Cu_2L^1)pz]$	1.49	2.03	−200		0.3	9
$[(Cu_2L^1)Me_2pz]$	1.56	2.00	−190	—	0.2	9
$[(Cu_2L^2)pz]\cdot H_2O$	1.38	2.00	−240	—	0.0	9
$[(Cu_2L^3)pz]$	1.33	1.92	−260	−82	0.1	8

[a] Intermolecular coupling parameter, $2J$ = singlet–triplet splitting; t.i.p. ($N\alpha$) = $60 \times 10^{-6}\ cm^3\ mol^{-1}$ per Cu. t.w. = this work. Errors in g; ±0.01, $2J$; ±2 cm^{-1}, % monomer; ±0.05.

Table 2. Cyclic voltammetric data for the polynuclear nickel(II) complexes of the unsymmetrical ligands H_6L and H_3L^3 in comparison with their symmetrical analogues incorporating H_3L^1 and H_3L^2

	Process I					Process II					
Compound	E_p^f	E_p^r	ΔE_p	$E_{1/2}$	i_p^a/i_p^c	E_p^f	E_p^r	ΔE_p	$E_{1/2}$	i_p^a/i_p^c	
$[Ni_4L(Me_2pz)_2]$ **(2)**	−2066	−1994	72	−2030	0.95	−2750	—	—	−2708	*	t.w.
$[Ni_2L^1(Me_2pz)]$	−2334	−2158	76	−2196	0.99	−2790	−2713	80	−2751	1.08	10
$[Ni_2L^2(Me_2Pz)]$	−2010	−1928	82	−1969	0.95	−2508	−2430	78	−2469	1.10	10
$[Ni_2L^3(Me_2Pz)]$	−2074	−1958	116	−2016	0.97	−2767	−2660	107	−2714	*	8

Experimental conditions: $\sim 1 \times 10^{-3}$ M solutions in DMF, 0.1 M TBAP supporting electrolyte, at a glassy carbon electrode, Pt wire auxiliary electrode, 100 mV sec^{-1} scan rate, AgCl reference electrode. Relative to the ferrocene/ferrocenium couple (0.572 V *vs* Ag/AgCl, DMF). E_p = peak potential (mV). i_p = peak height; ΔE_p = peak to peak separation; $E_{1/2}$ = half wave potential; Symbols f and r denote forward (cathodic) and (reverse) anodic processes; *poorly resolved anodic peak renders accurate measurement difficult; t.w. = this work.

poorly resolved anodic wave. OSWV and NPV measurements yielded $E_{1/2}$ values of −2.03 and −2.70 V for process I and II, respectively. As was the case noted previously [8] in the electrochemical behaviour of the dinuclear complexes of H_3L^3 under identical experimental conditions, process I occurs at a similar potential to that at which the initial reduction takes place within the symmetrical analogue, $[Ni_2L^2(Me_2Pz)]$, and may be ascribed to the reduction of the Ni^{II} ions situated at the salicylidene "ends" of the ligand. Process II may similarly be ascribed to the transfer of electrons at the Ni^{II} ions coordinated within the 1-methyl-3-oxobutenyl moiety. By virtue of the bis-binucleating nature of the ligand, electron transfer involves the passage of two electrons i.e. one electron to each similarly coordinated Ni^{II} ion and thus a total of four electrons are transferred to the tetranuclear complex. As was also found [8,10] to be the case within the electrochemistry of the analogous nickel(II) complexes incorporating H_3L^1 and H_3L^3, additional processes are apparent within the voltammetric scans in the present system. They have been previously assigned to the presence of freely interconverting chemically similar structural isomers and this is believed to be the case in the present system.

The successful incorporation of the bis-salicylaldehyde moiety within the current ligand framework provides the opportunity to develop extended molecular arrays built around this unit. Current research is concerned with the use of H_6L in conjunction with the dipyrazole entities; 4,4′-di-3,5-dimethylpyrazole (mdpz) and 4,4′-methylenebis(3,5-dimethylpyrazole) (mbdpz) [13] with the aim of producing higher order aggregates. It is possible to form "pair-of-tetramers", $[(M_4L)_2(mbdpz)_2]$, species as well as polymeric $[(M_4L)_n(mdpz)_n]$ complexes.

Acknowledgements—This work was supported by grants from the Australian Research Council to K.S.M.

REFERENCES

1. Guerriero, P., Tamburini, S. and Vigato, P. A., *Coord. Chem. Rev.* 1995, **139,** 17; Alexander, V., *Chem. Rev.* 1995, **95,** 273; Fenton, D. E. and Okawa, H., *J. Chem. Soc., Dalton Trans.* 1993, 1349; McKee, V., *Adv. Inorg. Chem.* 1993, **40,** 323.
2. *Metal Clusters in Proteins.* (Edited by L. Que, Jr), ACS Symposium Series: Vol. 372. American Chemical Society, Washington, D.C. (1988).
3. Stephen, D. W., *Coord. Chem. Rev.* 1989, **95,** 41; McKenzie, C. J. and Robson, R. J., *J. Chem. Soc., Chem. Commun.* 1988, 112; Wei, L., Bell, A., Ahn, K.-H., Holl, M. M., Warner, S., Williams, I. and Lippard, S. J., *Inorg. Chem.* 1990, **29,** 825; Poulton, J. T., Foulting, K. and Caulton, K. G., *Organometallics* 1992, **11,** 1364.
4. *Magneto-structural Correlations in Exchange Coupled Systems* (Edited by R. D. Willet, D. Gatteschi and O. Kahn). NATO ASI Series C, Vol. 140. D. Reidel, Dordrecht (1985); *Magnetic Molecular Materials* (Edited by D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio) Vol. 198; NATO ASI. Kluwer Academic, Dordrecht (1991); Kahn, O., *Molecular Magnetism.* VCH, New York (1993); Kahn, O., *Adv. Inorg. Chem.* 1995, **43,** 179; Murray, K. S., *Adv. Inorg. Chem.* 1995, **43,** 261.
5. McKee, V. and Tandon, S. S., *J. Chem. Soc., Dalton Trans.* 1991, 221; Kruger, P. E. and McKee, V., to be published.
6. Tandon, S. S., Thompson, L. K., Bridson, J. N. and Benelli, C., *Inorg Chem.* 1995, **34,** 5507; Kruger, P. E., Lingga, N. and McKee, V., to be published.
7. Tandon, S. S., Mandal, S. K., Thompson, L. K. and Hynes, R. C., *Inorg. Chem.* 1992, **31,** 2215.
8. Kruger, P. E., Moubaraki, B., Murray, K. S. and Tiekink, E. R. T., *J. Chem. Soc., Dalton Trans.* 1994, 2129.
9. Mazurek, W., Berry, K. J., Murray, K. S., O'Connor, M. J., Snow, M. R. and Wedd, A. G., *Inorg. Chem.* 1982, **21,** 3071; Mazurek, W., Kennedy,

B. J., Murray, K. S., O'Connor, M. J., Rodgers, J. R., Snow, M. R., Wedd, A. G. and Zwack, P. R., *Inorg. Chem.* 1985, **24,** 3258.

10. Mazurek, W., Bond, A. M., O'Connor, M. J. and Wedd, A. G., *Inorg. Chem.* 1986, **25,** 906.
11. Marvel, C. S. and Tarköy, N., *J. Am. Chem. Soc.* 1957, **79,** 6000.
12. Doman, T. N., Williams, D. E., Banks, J. F., Buchanan, R. M., Chang, H.-R., Webb, R. J. and Hendrickson, D. N., *Inorg. Chem.* 1990, **29,** 1058 and references therein.
13. Kruger, P. E., Fallon, G. D., Moubaraki, B. and Murray, K. S., *J. Chem. Soc., Chem. Commun.* 1992, 1726.