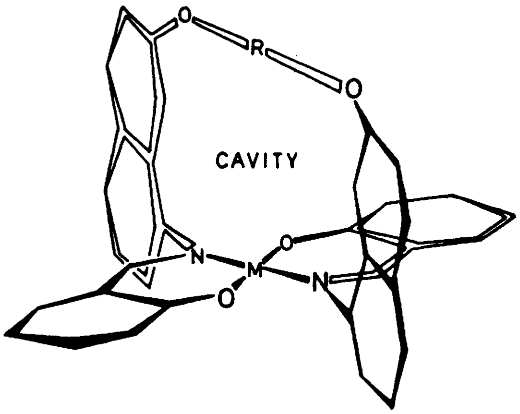
Sterically Hindered Co-ordination Sites in Metal Complexes. Part 1. The Synthesis and Properties of ' Capped ' Four-co-ordinate Metal Schiff-base Complexes

By **Alan R. Hendrickson, Janet M. Hope, and Raymond L. Martin,***† Research School of Chemistry
Australian National University, Canberra, Australia 2600

The synthesis of several sterically hindered N_2O_2 and N_4 ligands is described in which a quadridentate Schiff base is ' capped ' by condensation of salicylaldehyde or pyrrole-2-carbaldehyde with a series of bis(8-aminonaphthyl) n-alkyl diethers. A number of representative complexes have been prepared and characterized with the metal ions Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}. The n.m.r. spectrum of the neutral monomeric nickel(II) derivative is consistent with the proposed *trans* planar ' capped ' structure, a structure designed to provide for a study of the steric requirements of bonding to hindered metal-ion sites.

It is well known that in metal-containing systems of biological origin the active metal site is frequently shielded from nucleophilic or electrophilic attack by a protective and selective environment.[1] In these situations, a hydrophobic pocket around the metal ion is often provided by the neighbouring organic matrix which restricts access of undesirable entities and may also exert subtle conformational influences on the system. In this regard, the search for inorganic models which might mimic myoglobin or haemoglobin has led directly to the synthesis of sterically hindered ' picket fence '[2-4] and ' capped '[5-7] porphyrins in which the metal ion and its bonded oxygen molecule in the biological porphyrin environment are protected from further reaction to such an extent that reversible oxygenation can be observed. Unfortunately, detailed studies of the mechanisms of binding of small reactive molecules to transition-metal substrates is often inhibited by their aggregation to bridged oligomers which rapidly follow the initial adduct formation.[8] Accordingly, we have designed some multidentate ligands which combine the synthetic and structural versatility of Schiff bases together with the protective features displayed by biological and model porphyrin systems.



(I)

In this paper, syntheses of several sterically hindered Schiff bases and representative transition-metal complexes are described. The donor-atom set in the square-planar complexes is *trans*-N_2O_2 and a pronounced cavity has been introduced on one side of the N_2O_2 plane by the incorporation of naphthyl groups at both N atoms orthogonal to this plane. The cavity above the metal atom is closed by a ' fly-over ' bridge between the naphthyl groups comprised of a polymethylene diether link illustrated schematically in (I). The molecular and crystal structure of a nickel(II) complex formed with one of the new ' fly-over ' ligands is described in the following paper.[9]

EXPERIMENTAL

Syntheses.—*N-Acetyl-8-aminonaphth-2-ol.*[10] Acetic anhydride (9.0 g, 0.09 mol) was added dropwise and with vigorous stirring to 8-aminonaphth-2-ol (T.C.I., Japan) (4.8 g, 0.03 mol) and the mixture cooled in ice. After 10 min the solid was filtered off, washed with diethyl ether (100 cm^3), and recrystallized (with decolourizing carbon) from boiling water (300 cm^3) yielding white crystals (3.5 g, m.p. 199—201 °C).

2,2'-Tetramethylenedioxydi(N-*acetyl-8-aminonaphthalene*).—*N*-Acetyl-8-aminonaphth-2-ol (4.0 g, 0.02 mol) and sodium (0.46 g, 0.02 mol) were dissolved in dry ethanol (100 cm^3). 1,4-Dibromobutane (Eastman) (2.16 g, 0.01 mol) was added and the solution refluxed. After 1.5 h a white solid appeared and refluxing was continued for another 6 h. On cooling, the solid (m.p. 245 °C) was collected (3.0 g) and washed well with ethanol.

2,2'-Tetramethylenedioxydi(*8-aminonaphthalene*).— The above compound (2.4 g, 0.005 5 mol) and K[OH] (3.36 g, 0.06 mol) were refluxed in ethylene glycol (75 cm^3) for 4 h. The product, precipitated by adding ice to the warm solution, was recrystallized from either chloroform or dichloromethane (with decolourizing carbon). The volume of the solution was reduced and light petroleum (b.p. 60—80 °C) added until the first sign of cloudiness. On cooling, white light-sensitive needles separated (m.p. 99—104 °C).

2,2'-Tetramethylenedioxydi(*8-*N*-salicylideneiminonaphthalene*), H_2L^4.—A four-fold excess of salicylaldehyde was added to the hot ethylene glycol solution described above. After standing overnight, the product was precipitated by the addition of ice. The solid was dissolved in dichloromethane and purified by column chromatography with dichloromethane as eluant. The pure, yellow, crystalline Schiff base (m.p. 183—186 °C) was obtained on reduction of volume and addition of light petroleum (b.p. 60—80 °C).

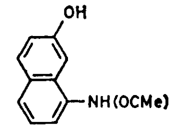
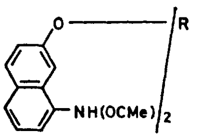
---

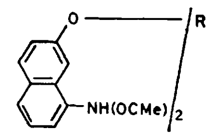
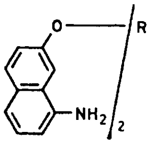
† *Present address*: Monash University, Clayton, Victoria, Australia 3168.

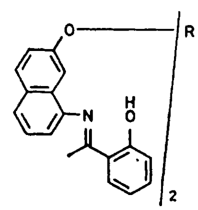
An analogous series of compounds in which the C_4H_8 bridge is replaced by C_6H_{12}, C_8H_{16}, and $C_{10}H_{20}$ respectively were prepared similarly from the respective dibromoalkanes (Pfaltz and Bauer). The general preparative data are presented in Table 1. The protonated Schiff-base ligands are abbreviated to H_2L^4, H_2L^6, H_2L^8, and H_2L^{10} where the superscripts 4, 6, 8, and 10 define the number of methylene groups in the 'fly-over' linkage.

TABLE 1

Details of syntheses

Product	R	Amount (g, mol) of reagent		Volume (cm³) of ethanol solvent	Amount (g, mol) of dibromoalkane	Reflux time (h)	Colour
			Sodium				
	C_4H_8	4.0, 0.02	0.46, 0.02	100	2.16, 0.01	7.5	White
	C_6H_{12}	4.1, 0.02	0.46, 0.02	100	2.5, 0.01	2	White
	C_8H_{16}	4.0, 0.02	0.46, 0.02	50	2.8, 0.01	2	White
	$C_{10}H_{20}$	4.0, 0.02	0.46, 0.02	50	3.0, 0.01	3	White

Product	R		K[OH]	Volume (cm³) of ethylene glycol solvent [a]	Colour	M.p. (θc/°C)
	C_4H_8	2.4, 0.006	3.36, 0.06	75	White	99—104
	C_6H_{12}	2.6, 0.005	3.0, 0.05	100	White	118—120
	C_8H_{16}	2.8, 0.005	3.1, 0.06	30	Pinkish	
	$C_{10}H_{20}$	9.8, 0.02	9.6, 0.2	75	White	140

Product	R	Purification [b] Colour	M.p. (θc/°C)	Recrystallization solvent
	C_4H_8	Yellow	183—186	CH_2Cl_2–light petroleum
	C_6H_{12}	Yellow	146—148	CH_2Cl_2–EtOH
	C_8H_{16}	Yellow	104—106	CH_2Cl_2–light petroleum
	$C_{10}H_{20}$	Yellow	112	CH_2Cl_2–light petroleum

[a] All reactions refluxed for 4 h; the recrystallization solvent was CH_2Cl_2–light petroleum. [b] By chromatography over SiO_2 in CH_2Cl_2.

2,2′-Tetramethylenedioxydi(8-N′-*pyrrol-2-ylmethyleneiminonaphthalene*).— 2,2′-Tetramethylenedioxydi(8-aminonaphthalene) (0.74 g) and pyrrole-2-carbaldehyde (0.84 g) were dissolved in CH_2Cl_2 (50 cm³) and the solution stirred over molecular sieves at room temperature for 24 h. Following filtration and evaporation of the solvent, the product (m.p. 85 °C) was recrystallized from CH_2Cl_2–light petroleum. N.m.r. in $CDCl_3$: OCH_2 [4.23(m)], CH_2 [2.01(m)], pyrrole [5.84(br), 5.98(m), 6.58(m)], naphthyl (7.0—7.8), CH [8.27(s)]; integration showed that *ca.* 2 mol of CH_2Cl_2 are present in the lattice (Found: C, 60.3; H, 4.9; N, 7.4. Calc. for $C_{34}H_{30}N_4O_2\cdot 2.3\,CH_2Cl_2$: C, 60.4; N, 4.8; N, 7.8%). Mass spectrum: m/e 526 (M^+), 447, 235, 115, and 80.

[*2,2′-Tetramethylenedioxydi*(8-N-*salicylideneiminonaphthalenato*) (2—)]*nickel*(II), [NiL^4].—Nickel(II) acetate tetrahydrate (0.25 g, 0.001 mol) was refluxed in EtOH (50 cm³) with H_2L^4 (0.58 g, 0.001 mol) for 1.5 h. Olive-green needles separate on cooling. Pure [NiL^4], obtained by chromatography on SiO_2 with CH_2Cl_2, was recrystallized as green crystals (m.p. 310—315 °C) from CH_2Cl_2 by addition of light petroleum.

[NiL^4(bipy)].—2,2′-Bipyridyl (0.08 g, 0.5 mmol) was added with stirring to a warm solution of [NiL^4] (0.31 g, 0.05 mmol) in dichloromethane (30 cm³). The gold-brown solution was filtered and light petroleum (b.p. 30—40 °C) added until the product precipitated. The yellowish solid was collected and air dried (m.p. 250 °C).

[NiL^4(phen)].—1,10-Phenanthroline (0.04 g, 0.02 mmol) was added with stirring to a warm solution of [NiL^4] (0.13 g, 0.2 mmol) in dichloromethane (20 cm³). The yellow solution was filtered, cooled in ice, and light petroleum (b.p. 30—40 °C, 40 cm³) was added with stirring. The yellow solid was collected and air dried (m.p. 260 °C).

[CuL^4].—(*i*) The Schiff base H_2L^4 (0.58 g, 0.001 mol) was refluxed with copper(II) acetate monohydrate (0.19 g, 0.001 mol) in ethanol (50 cm³) for 1.5 h. The dark brown crystals which separated from the hot solution were purified and recrystallized (m.p. 285—288 °C) as described for the nickel complex.

(*ii*) 2,2′-Tetramethylenedioxydi(8-aminonaphthalene) (0.5 g, 0.001 3 mol) was refluxed with bis(salicylaldehydato)-

copper(II) for 1.5 h. The dark crystals which separated were collected and purified by column chromatography using a CH_2Cl_2 eluant as described above.

$[(ZnL^4)_n]$.—The Schiff base H_2L^4 (0.58 g, 0.001 mol) was refluxed with $Zn[O_2CMe]_2 \cdot 2H_2O$ (0.21 g, 0.001 mol) in ethanol (75 cm^3) for 1.5 h. The yellow solid was collected and washed with hot $CHCl_3$ (100 cm^3).

$[(CoL^4)_n]$.—Cobalt(II) acetate tetrahydrate (0.25 g, 0.001 mol) and H_2L^4 (0.58 g, 0.001 mol) were refluxed in ethanol (50 cm^3) for 2 h. The resulting red solid was collected and washed with ethanol. The crystals (m.p. 330 °C) were relatively insoluble in $CHCl_3$, CH_2Cl_2, benzene, and dimethyl sulphoxide (dmso).

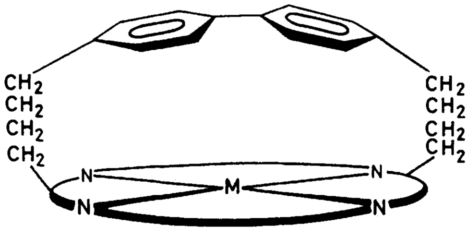
$[CoL^4]$.—The polymer $[(CoL^4)_n]$ was dissolved in a minimum volume of boiling pyridine. The solution was filtered and the product precipitated with ice, collected, and dried. This complex was recrystallized (m.p. 315—318 °C) from CH_2Cl_2–light petroleum (b.p. 80—100 °C).

$[FeL^4]$.—The Schiff base H_2L^4 (0.58 g, 0.001 mol) was refluxed in ethanol (75 cm^3) under N_2 for 15 min; $FeCl_2 \cdot 4H_2O$ (0.198 g, 0.001 mol) was added to the refluxing solution followed by piperidine (1 cm^3). The solution turned deep red and refluxing was continued for 7 h under N_2. The red solid that formed was filtered off and extracted into dichloromethane. The volume of the solution was reduced and ethanol added. The red crystals were collected and dried in air.

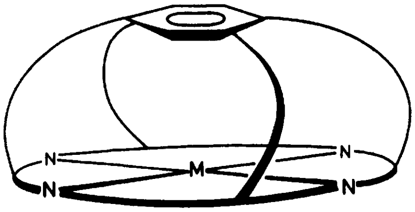
Physical Measurements.—The following instruments were used: Cary 14 spectrophotometer for electronic transmission spectra, Beckman DK-2 instrument for diffuse-reflectance spectra on powdered solid samples; Varian HA-100 (100 MHz) for ^1H n.m.r. spectra; A.E.I. MS902 mass spectrometer; Perkin-Elmer 457 i.r. spectrophotometer, samples being supported in KBr discs.

RESULTS AND DISCUSSION

To date, the constructions of a non-co-ordinating protecting group across a co-ordination site of a metal ion have been based on a porphyrin ring and, of necessity, had their foundations attached well out on the periphery of the molecule [*cf.* (II)]. In order to restrict the dimensions of the cavity, we have designed the ' fly-over ' in such a manner that the take-off point is actually at the ligating atoms. To avoid the ' floppy ' nature of a saturated carbon chain, we have employed rigid, planar, α-naphthyl groups to support the polymethylene ether capping unit above the metal ion. Furthermore, examination of models and the crystallographic evidence[11] available for complexes of aryl-substituted Schiff bases suggested that the α-naphthyl units would stand perpendicular to the salicyl basal plane. These features were incorporated in the Schiff-base ligand shown in (I). A degree of flexibility in the dimensions of the cavity is attainable through the choice of R with (*i*) the length of R dictating the maximum separation of the two linked naphthyl groups, and (*ii*) the possibility of branched alkyl chains or substituted aromatic groups providing a variable degree of protection over the cavity perpendicular to the –O–R–O– direction but parallel to the MN_2O_2 basal plane.

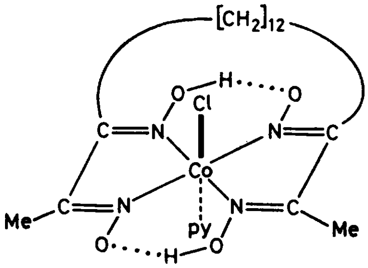


(II) ref. 5



(III) refs. 6 and 7

Some previous complexes of Schiff bases have incorporated a variable-length alkyl link between the two nitrogens ranging from the ethylenediamine link (C_2) to C_{12}, compared with the 14—20 atoms in the present ligands. In the former examples, of those complexes which are monomeric, it is not clear whether the longer-chain non-polymeric complexes have *cis* or *trans* nitrogen atoms.[12,13] By design, the contrasting feature with the present species is that the nitrogen donors ***must*** be *trans* if the co-ordination geometry is square planar. A further example of a *cis*-C_{14} link is provided by the cobaloxime (IV)[14] and as confirmed by *X*-ray crystallography[15] the bridge lies to the side of the Cl–Co–py axis.

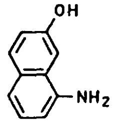
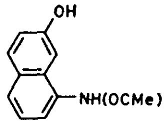
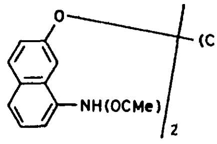
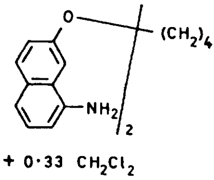


(IV)

Synthesis of the new quadridentate ligand based on salicylaldehyde, as illustrated schematically in the Scheme, is relatively conventional but requires protection of the amino-group prior to alkylation and linking of the two naphthol units. A series of ligands has been synthesized *via* this general scheme in which R represents the straight-chain alkyl groups C_4H_8, C_6H_{12}, C_8H_{16}, and $C_{10}H_{20}$. The deprotonated quadridentate Schiff-base ligands are abbreviated for convenience to $[L^4]^{2-}$, $[L^6]^{2-}$, $[L^8]^{2-}$, and $[L^{10}]^{2-}$ respectively, with the numerical superscript indicating the number of carbon atoms in the alkyl ' fly-over '. Analytical, mass spectral, and n.m.r. spectral data are provided in Table 2.

TABLE 2

Analytical data, n.m.r. spectra, and mass spectra for bases

Compound	Analysis (%)[a]			Chemical shift ($\delta = 0$ for $SiMe_4$)							Parent peak
	C	H	N	OCH_2—	—CH_2—	—CH_2—CH_2—CH_2—	aromatic	OH	NH	Solvent	(*m*/*e*)
							6.5—7.7	9.42 (br)	5.22 (s)	$S(CD_3)_2O$	
	71.2 (71.6)	5.6 (5.5)	6.7 (7.0)			[CH_3, 2.14 (s)]	7.0—7.8	9.72 (br)	?	$S(CD_3)_2O$	201
	72.8 (73.7)	6.3 (6.2)	5.8 (6.1)	4.22 (m)	2.03 (m)	[CH_3, 2.18 (s)]	7.1—7.9		?	$S(CD_3)_2O$	456
	73.2 (72.9)	6.4 (6.2)	6.7 (7.0)	4.14 (m)	2.06 (q)	[0.33 CH_2Cl_2, 5.23]	6.7—7.8		3.91	$CDCl_3$	372
Amine 6[c]	77.6 (78.0)	7.0 (7.0)	6.5 (7.0)	4.08 (t)	1.90 (m)	1.66 (m)	6.7—7.8		*ca.* 3.8	$CDCl_3$	
Amine 8	78.4 (78.5)	7.7 (7.5)	6.4 (6.5)	4.07 (t)	1.86 (m)	1.48 (br)	6.7—7.8		3.9	$CDCl_3$	
Amine 10	78.5 (78.9)	7.7 (7.9)	5.8 (6.1)	4.07 (t)	1.85 (m)	1.40 (m)	6.7—7.8		3.9	$CDCl_3$	456
									CH		
H_2L^4[d]	77.2 (78.6)	5.3 (5.6)	4.6 (4.8)	4.20 (m)	2.08 (m)		6.8—7.8	13.39 (s)	8.68 (s)	$CDCl_3$	580
H_2L^6	79.1 (78.9)	5.9 (6.0)	4.3 (4.6)	4.09 (t)	1.88 (m)	1.62 (m)	6.8—7.8	13.33 (s)	8.66 (s)	$CDCl_3$	608
H_2L^8	78.7 (79.2)	6.3 (6.3)	3.9 (4.4)	4.08 (t)	1.83 (m)	1.45 (m)	6.8—7.8	13.34 (s)	8.69 (s)	$CDCl_3$	636
H_2L^{10}	79.2 (79.5)	6.7 (6.7)	4.0 (4.2)	4.08 (t)	1.83 (m)	1.37 (m)	6.8—7.8	13.34 (s)	8.66 (s)	$CDCl_3$	664

[a] Calculated values are given in parentheses. [b] Amine 4. [c] As amine 4 with $(CH_2)_6$ instead of $(CH_2)_4$. [d] Solution molecular weight (vapour-pressure osmometry in $CHCl_3$, 37 °C) 594; calc. 581.

Representative complexes of $[L^4]^{2-}$ have been prepared with the metal ions Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} (Table 3).

The red cobalt(II) complex isolated from the reaction mixture analyzes for the 1 : 1 compound, CoL^4. It is insoluble and presumably polymeric with the attachment of the ligand to more than one metal ion. However, the polymer can be converted into a monomer by dissolution of the polymer in pyridine and subsequent isolation of an orange complex by dilution of the pyridine solution with water. The resulting cobalt(II) complex, $[CoL^4]$, is air stable, soluble, and monomeric as shown by mass spectrometry.

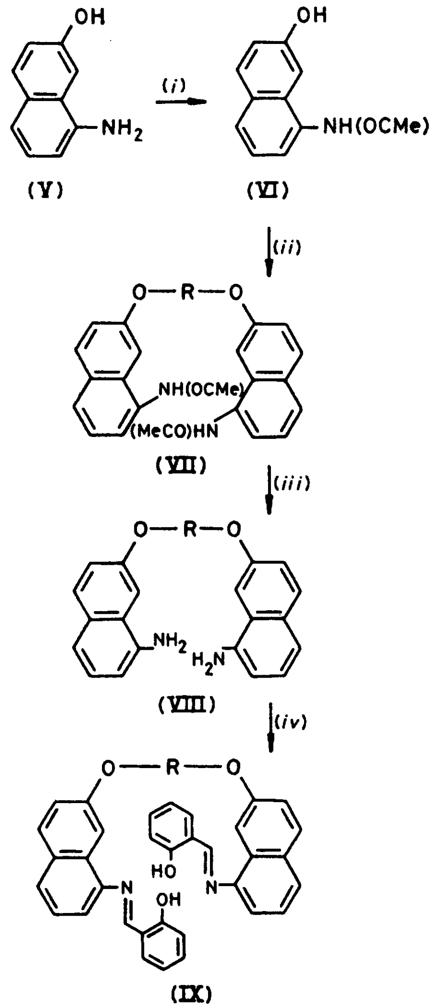
The green copper(II) complex, $[CuL^4]$, has been synthesized from $Cu[O_2CMe]_2$ and the protonated ligand as well as from bis(salicylaldehydato)copper(II) and 2,2′-tetramethylenedioxydi(8-aminonaphthalene). The complex is monomeric and presumably square planar. We have been unable to isolate pyridine adducts of this complex.

Due to its insoluble nature, the zinc(II) complex, ZnL^4, is considered to be polymeric. An attempt to convert the complex into a monomer, by the pyridine procedure which proved effective for $[CoL^4]$, resulted in displacement of the zinc(II) ion and recovery of the protonated ligand H_2L^4.

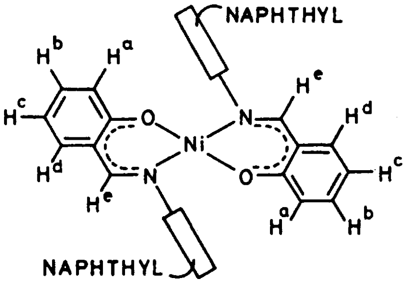
With Ni^{II}, no evidence was obtained for polymeric species and all the spectroscopic evidence suggested that the complex is monomeric and square-planar as designed (I). The n.m.r. spectrum of $[NiL^4]$ possesses some unusual and interesting features (Figure). First, the OCH_2 resonance at δ *ca.* 4.5 appears as an AB quartet coupled to the adjoining CH_2 unit. Raising the temperature from -40 to $+55$ °C decreases the chemical-shift difference between the protons although the AB quartet does not collapse. Decoupling of the adjacent

CH_2 unit (219 Hz) shows the AB quartet ($J = 9$ Hz) with a superimposed beat on one resonance (Figure).

The unusually large upfield shift on complexation for two of the aromatic protons apparently arises from the proximity of H^a and, to a lesser extent, H^b to the perpendicular π system of the adjacent naphthyl group (X). This interaction leads to an unusually well spread n.m.r. spectrum and allows assignment of all the salicyl protons in $CDCl_3$ at 55 °C: CH_2CH_2 (2.21); OCH_2 (4.56); H^a (5.22); H^b (6.28); H^c (6.75); H^d (6.92); H^e (8.83); naphthyl (7.1—7.8). In spin-decoupling experiments irradiation at H^b (629 Hz) furnishes the H^a resonance as a singlet and irradiation at H^d (693 Hz) affords the H^e resonance also as a singlet. Further decoupling was uninformative due to beats.



SCHEME (*i*) Acetic anhydride; (*ii*) (*a*) Na(OEt), (*b*) BrRBr; (*iii*) K[OH]–ethylene glycol; (*iv*) salicylaldehyde



(X)

The possibility of disrupting the NiN_2O_2 plane by co-ordination to aromatic nitrogenous chelating bases was confirmed by the formation of phenanthrolene (phen) and bipyridyl (bipy) adducts of $[NiL^4]$. These complexes are presumably six-co-ordinate as evidenced by the electronic transitions at 950 nm ($\varepsilon = 19$ dm^3 mol^{-1} cm^{-1}) for $[NiL^4(bipy)]$ and 945 nm ($\varepsilon = 21$ dm^3 mol^{-1} cm^{-1}) for $[NiL^4(phen)]$ in CH_2Cl_2 solution.

The *cis* configuration imposed by these chelating bases suggests that the NiN_2O_2 core is stereochemically flexible. With the unidentate base 1-methylimidazole (mim) the adduct isolated is the six-co-ordinate bis-adduct with spectral features similar to the phen and bipy adducts, *i.e.* $[NiL^4(mim)_2]$ remains six-co-ordinate in CH_2Cl_2 solution. In the presence of pyridine, the only adduct isolated from solution was the five-co-ordinate mono adduct $[NiL^4(py)]$, although in pure pyridine an addi-

TABLE 3

Analytical, molecular-weight, and mass-spectral data for complexes

Complex	Analysis (%) [a] C	H	N	Parent peak [b] in mass spectrum (*m*/*e*)
$[NiL^4]$ [c]	71.1 (71.6)	4.8 (4.7)	4.1 (4.4)	636
$[NiL^4(phen)]$	72.9 (73.5)	4.9 (4.7)	6.7 (6.9)	636 [d] $[NiL^4]$
$[NiL^4(bipy)]$	72.1 (72.6)	4.9 (4.8)	6.9 (7.1)	636 [d] $[NiL^4]$
$[NiL^4(mim)_2]$	69.3 (68.9)	5.3 (5.3)	10.1 (10.5)	
$[NiL^4(py)]$	72.1 (72.1)	5.1 (4.9)	5.4 (5.9)	
$[CuL^4]$ [e]	71.1 (71.1)	4.8 (4.7)	4.1 (4.4)	641
$[(ZnL^4)_n]$	71.2 (70.9)	4.8 (4.7)	4.1 (4.4)	
$[FeL^4]$	71.6 (71.9)	4.7 (4.8)	4.4 (4.4)	634
$[(CoL^4)_n]$	70.7 (71.6)	5.2 (4.7)	4.3 (4.4)	
$[CoL^4]$	72.2 (71.6)	4.8 (4.7)	4.4 (4.4)	637
$[CoL^{10}]$	73.8 (73.2)	6.1 (5.9)	3.9 (3.9)	721

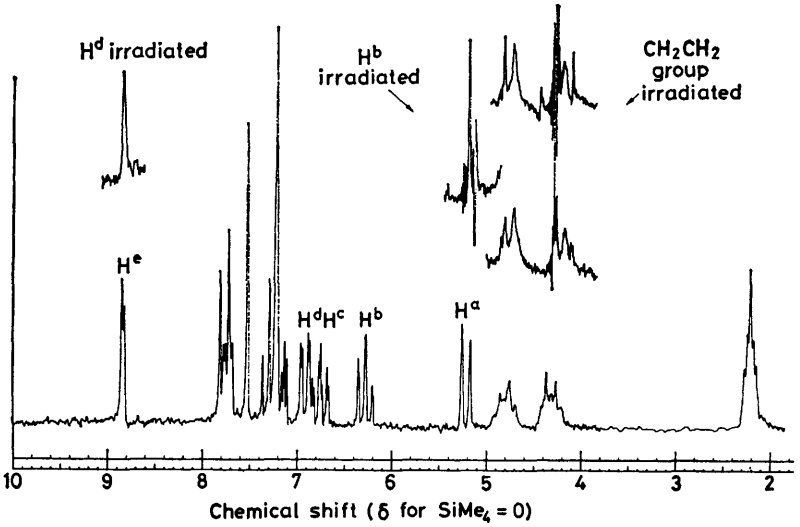
[a] Calculated values are given in parentheses. [b] Taken for most abundant metal isotope. [c] Solution molecular weight (vapour-pressure osmometry in $CHCl_3$, 37 °C) 624; calc. 637. [d] Parent peak due to adducts not observed. [e] Solution molecular weight (vapour-pressure osmometry in $CHCl_3$, 37 °C) 648; calc. 642.

TABLE 4

Electronic-spectral data (nm) for four-, five-, and six-co-ordinate $[NiL^4]$ complexes

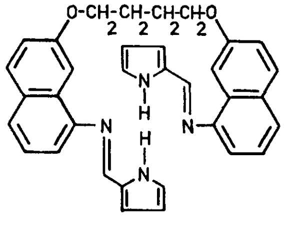
Compound	Diffuse reflectance [a]		Solution spectra [b]		
$[NiL^4]$			620		
$[NiL^4(mim)_2]$	(590)	970	*c*	968	
$[NiL^4(py)]$	(600)		*c*		1 890
$[NiL^4(py)_2]$			*c*	995 [d]	
$[NiL^4(bipy)]$	(580)	940	(580)	950	
$[NiL^4(phen)]$			(575)	945	

[a] Powdered sample, Beckman DK-2 instrument; i.r. overtone bands obscure 1 500—2 500 nm region. [b] In CH_2Cl_2 solution. [c] Not measured in this region. [d] Spectrum obtained in pure pyridine.



N.m.r. spectrum of [NiL^4] in CDCl$_3$. The two decoupled spectra of the OCH$_2$ resonance were obtained under slightly different experimental conditions in an attempt to provide improved resolution and eliminate the beat

tional pyridine molecule co-ordinates to afford the six-co-ordinate bis adduct (Table 4). For the less stable six-co-ordinate adducts the absorption at *ca.* 970 nm is moved to lower energy. To ascertain the exact conformation and spatial requirements of these new ligands, the single-crystal *X*-ray structure of [NiL^4] was determined. In addition to confirming the monomeric structure, knowledge and the dimensions and stereochemistry of the ' cavity ' provide an indication of the molecules which might, in principal, be accommodated in the available space. Details of the structure are described in the following paper.[9]



(XI)

The concept presented in this work is being extended in order to bring the redox potentials of the complexes to values compatible with those exhibited by related biological molecules. As one extension into the various N_2Y_2 co-ordination combinations, the N_4 chelate (XI) has been prepared and characterized, although acceptable analytical data have not been obtained for its metal complexes (Experimental section).

[8/667 *Received, 10th April, 1978*]

REFERENCES

[1] F. Basolo, B. M. Hoffman, and J. A. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384.

[2] J. P. Collman, R. R. Gange, T. R. Halbert, J.-C. Marchon, and C. A. Reed, *J. Amer. Chem. Soc.*, 1973, **95**, 7868.

[3] J. P. Collman, R. R. Gange, and C. A. Reed, *J. Amer. Chem. Soc.*, 1974, **96**, 2629.

[4] J. P. Collman, R. R. Gange, J. Kouba, and H. Ljusberg-Wahren, *J. Amer. Chem. Soc.*, 1974, **96**, 6800.

[5] H. Diekmann, C. K. Chang, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1971, **93**, 4068.

[6] J. Almog, J. E. Baldwin, R. L. Dyer, and M. Peters, *J. Amer. Chem. Soc.*, 1975, **97**, 226.

[7] J. Almog, J. E. Baldwin, and J. Huff, *J. Amer. Chem. Soc.*, 1975, **97**, 227.

[8] J. E. Davies and B. M. Gatehouse, *Acta Cryst.*, 1973, **B29**, 2651.

[9] A. T. Baker, R. L. Martin, and D. Taylor, following paper.

[10] F. Kehrmann and E. F. Engelke, *Ber.*, 1909, **42**, 350.

[11] L. Wei, R. M. Stogsdill, and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 1058.

[12] W. C. Hoyt and G. W. Everett, jun., *Inorg. Chem.*, 1969, **8**, 2013.

[13] G. M. Mockler, G. W. Chaffey, E. Sinn, and H. Wong, *Inorg. Chem.*, 1972, **11**, 1308.

[14] J. Rétey, *Helv. Chim. Acta*, 1971, **54**, 2747.

[15] M. W. Bartlett and J. D. Dunitz, *Helv. Chim. Acta*, 1971, **54**, 2753.