Non-template Synthesis of New Tetra-aza Macrocyclic Ligands and their Cobalt, Nickel, and Copper Complexes: *X*-Ray Structure † of (5,14,15,16,17,18-Hexahydro-7-methyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecinato)nickel(II) Monoperchlorate

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Reaction of the open-chain tetramines 1,3-bis(*o*-aminophenylamino)propane (L) or 1,3-bis(*o*-amino-*p*-methylphenylamino)propane (L′) with 3-ethoxy-2-methylacrolein gives the title macrocycle, HL^1, or its methyl substituted derivative, HL^2, in yields of the order of 40% without recourse to either high dilution or metal template techniques. Reaction of HL^1 or HL^2 with Co^{II}, Ni^{II}, or Cu^{II} salts is accompanied by deprotonation of the ligand and its co-ordination to the metal ion as a monoanionic species. The *X*-ray structure of $[NiL^1][ClO_4]$ (1) confirms the site of deprotonation and establishes the square planar geometry of the metal ion. Treatment of $[NiL^1][ClO_4]$ with NEt_3 in air results in oxidative dehydrogenation of the ligand and the isolation of $[Ni(C_{19}H_{16}N_4)]$. Crystals of (1) are triclinic, space group $P\bar{1}$, with $a = 12.351(3)$, $b = 10.596(3)$, $c = 7.841(3)$ Å, $\alpha = 91.971(3)$, $\beta = 92.654(3)$, $\gamma = 108.978(3)°$, and $Z = 2$.

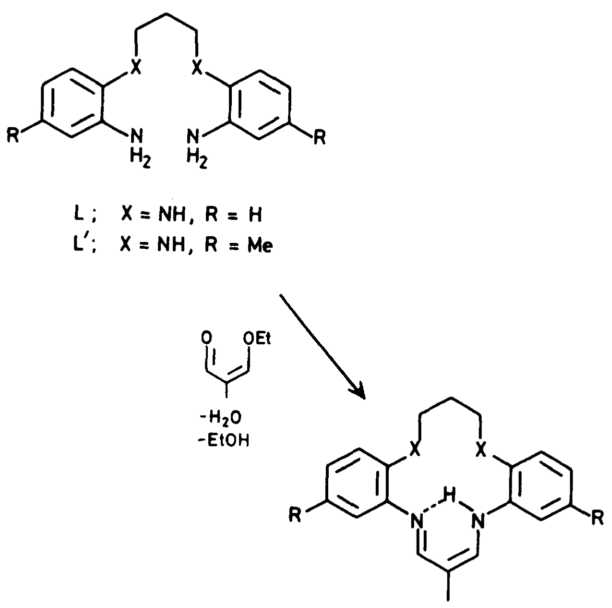
Recently, Breitmaier and Behr [1] reported the synthesis of the metal-free macrocycles HL^3 and HL^4 containing O_2N_2 or S_2N_2 donor sets. We have extended this synthetic procedure to yield the tetra-aza macrocycles HL^1 and HL^2 and investigated some aspects of the chemistry of the complexes with Co, Ni, and Cu.

Discussion

(*a*) *Free Macrocycles.*—The tetramines L or L′ [2] react with 3-ethoxy-2-methylacrolein to give good yields of the air-stable macrocyclic ligands. That they are formed without the presence of a metal ion or the use of high dilution techniques may be ascribed in part to the ability of both precursors and product to form stabilising intramolecular H bonds. This phenomenon has been invoked previously [3] to explain the formation of metal-free macrocyclic imines. Also of potential importance is the relatively unstrained nature of the product, *e.g.* ligand H_2L^5 may be formed free of a metal ion,[4] but H_2L^6 cannot be made in the absence of a metal.[5] *X*-Ray studies have shown [6] significant steric interaction between the Me groups and Ph rings of H_2L^6, reducing the planarity of the ligand and straining the structure.

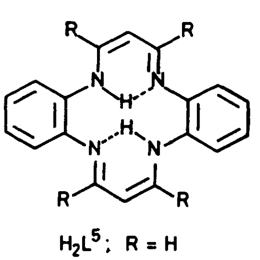
(*b*) *Metal Complexes.*—Reaction of HL^1 or HL^2 with Ni^{II} or Cu^{II} ions gave in each case the monoanionic chelates $[ML^1]^+$ or $[ML^2]^+$. The following structural determination of $[NiL^1][ClO_4]$ (1) confirms the site of ligand deprotonation as the acrolein-derived segment. The e.s.r. spectrum of $[CuL^1][BF_4]\cdot H_2O$ as a CH_2Cl_2 glass at 77 K gave spectral parameters similar to those reported [7] for square planar Cu^{II} complexes of other macrocyclic systems ($g_x = 2.1223$, $g_y = 2.0470$, $g_z = 1.9678$, $|A_{\parallel}| = 200$ G). In each attempt to isolate Co^{II} complexes, green precipitates of the octahedral Co^{III} species $[Co(L^1)X_2]$ or $[Co(L^2)X_2]$ (X = Cl or NCS) were obtained.

Treatment of a methanol solution of $[NiL^1][ClO_4]$ (1) with



L; X = NH, R = H
L′; X = NH, R = Me

HL^1; X = NH, R = H
HL^2; X = NH, R = Me
HL^3; X = O, R = H
HL^4; X = S, R = H



H_2L^5; R = H
H_2L^6; R = Me

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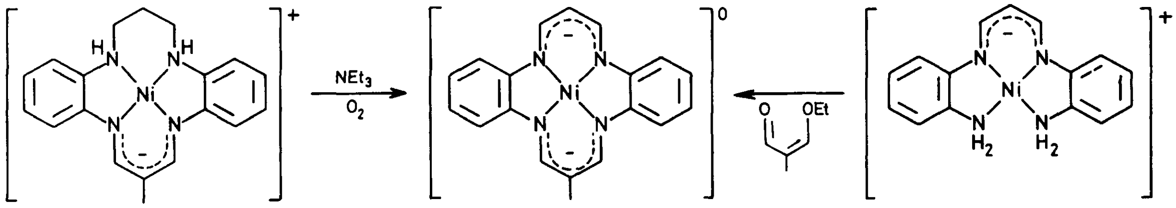
† *Supplementary data available* (No. SUP 23365, 43 pp.): observed and calculated structure factors, thermal parameters, least-squares planes, full list of atomic co-ordinates, bond distances and angles. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: 1 G = 10^{-4} T.



(1) (2) (3)

an excess of NEt_3 in air gives a red complex of stoicheiometry [$Ni(C_{19}H_{16}N_4)$]. The reaction does not proceed in the absence of air and the i.r. spectrum of the product shows the loss of both NH protons and also of the ClO_4^- counter ion. A report has appeared [8] of the oxidative dehydrogenation of a propane chain in other macrocyclic species under similar conditions. Strong evidence for the dehydrogenation of [NiL^1][ClO_4] (1) to (2) is provided by its alternative synthesis *via* (3), a precursor in which the C_3 backbone is already unsaturated. The Ni complex (3) is a known precursor [9] for Ni dibenzotetra-aza [14]annulenes. Reaction of (3) with 3-ethoxy-2-methylacrolein gives a quantitative yield of a compound identical to that derived from the action of NEt_3 on [NiL^1][ClO_4] (1). Work is continuing to establish the generality of the oxidative dehydrogenation of HL^1 and HL^2.

(*c*) *Description of the Structure of* [NiL^1][ClO_4] (1).—The Ni has a square planar stereochemistry, being bound to all four N atoms of the macrocycle. These five atoms are coplanar to within 0.04 Å. The Figure is a diagram of the cation. As expected, the bond lengths to N(1) and N(3) are 0.01 Å shorter than those to N(2) and N(4) [*ca.* 1.83(1) and 1.93(1) Å respectively]. Both values are in the typical range [10] for low-spin Ni–N bonds in these particular environments. The segment N(1)–C(19)–C(1)–C(2)–C(3)–N(3) is charge-delocalised and proton loss has occurred from the nitrogen atom of this section. The deviations from coplanarity of the two Ph rings and the charge-delocalised segment are small in comparison with those seen in the complexes of H_2L^6.[6] This is presumed to be due to the lesser effect of steric interaction here between H(3) and H(5) and between H(17) and H(19) (contact distances 2.051 and 2.086 Å respectively) compared to that between the larger Me groups and Ph rings of H_2L^6. The mean planes of the Ph rings intersect the mean plane of the *N*-donor set at angles of 3.6 and 7.1°, forming a shallow dome. The charge-delocalised segment deviates from coplanarity with the N(4) plane by 6.4°, on the opposite side to the Ph rings. The ' saddle ' geometry of H_2L^6 and its complexes is thus partially evident here, albeit on a much reduced scale. The Ni atom and the aliphatic chain N(4)–C(10)–C(11)–C(12)–N(2) adopt a ' chair ' configuration, expected for an unsaturated six-membered chelate ring.

Experimental

The tetramines L and L′ were prepared by published procedures.[2] 3-Ethoxy-2-methylacrolein was purchased from Fluka and used without further purification. Analytical data for the macrocyclic chelates are shown in Table 1.

(*a*) *Macrocyclic Ligands.*—3-Ethoxy-2-methylacrolein (1.1 cm^3, 10 mmol) was added to a refluxing solution of the tetramine L (2.6 g, 10 mmol) in toluene (90 cm^3). The solution was heated under reflux for 2 h, during which time it became deep orange. Evaporation under reduced pressure gave an oil which crystallised on trituration with a little cold MeOH. The orange microcrystals of HL^1 (1.2 g, 40%) were collected and recrystallised from boiling MeOH, m.p. 192—194 °C (Found: C, 74.2; H, 7.0, N, 18.3. $C_{19}H_{22}N_4$ requires C, 74.5; H, 7.2; N, 18.3%); mass spectrum: 306 (M^+). Ligand HL^2 was similarly prepared in 45% yield as fine orange needles, m.p. 144—146 °C (Found: C, 74.3; H, 7.5; N, 16.5. $C_{21}H_{26}N_4$ requires C, 74.6; H, 7.7; N, 16.6%); mass spectrum: 338 (M^+).

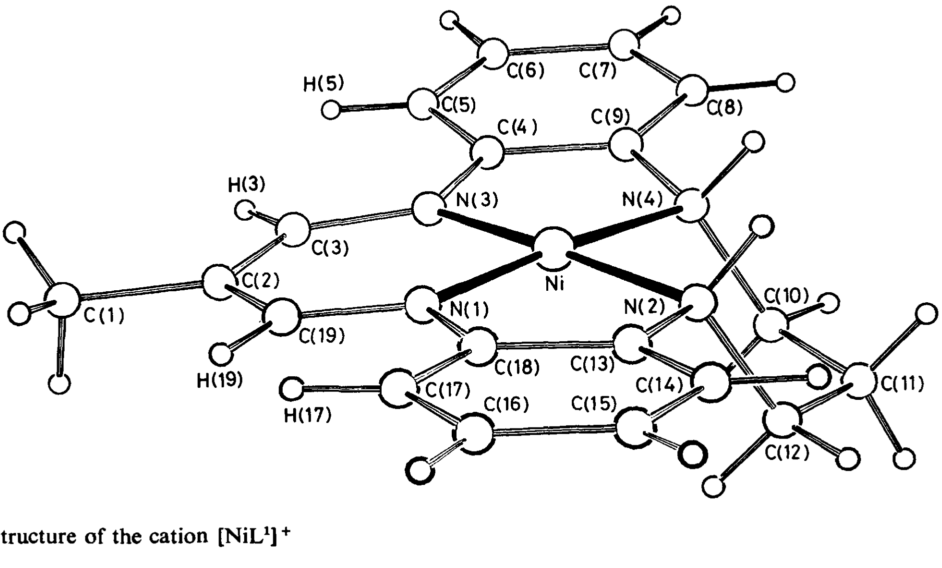


Figure. Molecular structure of the cation [NiL^1]$^+$

Table 1. Analytical data for the macrocyclic chelates

	Found (%)			Calculated (%)		
	C	H	N	C	H	N
$[NiL^1][ClO_4]$	49.0	4.4	11.8	49.2	4.5	12.1
$[NiL^1][BF_4]\cdot H_2O$	49.7	4.6	12.6	49.6	5.0	12.2
$[NiL^1]Cl\cdot 2H_2O$	52.3	5.3	12.5	52.3	5.7	12.8
$[NiL^2][BF_4]\cdot H_2O$	52.0	4.9	11.6	51.7	5.5	11.5
$[NiL^2]Cl\cdot H_2O$	56.5	6.0	12.3	56.7	6.1	12.6
$[Co(L^1)(NCS)_2]$	52.8	4.4	17.4	52.5	4.4	17.5
$[Co(L^1)Cl_2]$	52.0	4.6	12.9	52.4	4.8	12.9
$[Co(L^2)(NCS)_2]$	53.6	4.1	10.8	53.9	4.1	10.9
$[Co(L^2)Cl_2]$	54.3	4.4	11.7	54.0	4.5	12.0
$[CuL^1][ClO_4]\cdot 2H_2O$	45.0	5.2	10.8	45.2	4.9	11.1
$[CuL^1][BF_4]\cdot H_2O$	49.0	4.8	12.0	49.1	5.0	12.1
$[CuL^2][BF_4]\cdot H_2O$	48.0	4.6	11.7	48.2	4.9	11.8

Table 2. Selected bond lengths and angles * for $[NiL^1]^+$

(*a*) Bond lengths (Å)

Ni-N(1)	1.835(8)	Ni-N(3)	1.831(6)
Ni-N(2)	1.933(6)	Ni-N(4)	1.925(8)
C(2)-C(3)	1.384(15)	C(2)-C(19)	1.387(12)
C(3)-N(3)	1.339(11)	C(19)-N(1)	1.332(11)
N(3)-C(4)	1.406(13)	N(1)-C(18)	1.422(11)
C(4)-C(9)	1.388(12)	C(18)-C(13)	1.377(13)
C(9)-N(4)	1.446(10)	C(13)-N(2)	1.452(13)
N(4)-C(10)	1.507(11)	N(2)-C(12)	1.494(12)
C(10)-C(11)	1.522(12)	C(12)-C(11)	1.506(16)

(*b*) Bond angles (°)

N(1)-Ni-N(2)	86.6(3)	N(3)-Ni-N(4)	86.4(3)
C(2)-C(3)-N(3)	125.3(7)	C(2)-C(19)-N(1)	125.6(9)
C(3)-N(3)-C(4)	119.2(7)	C(19)-N(1)-C(18)	120.3(8)
Ni-N(3)-C(4)	114.7(5)	Ni-N(1)-C(18)	113.8(6)
C(9)-N(4)-Ni	109.6(5)	C(13)-N(2)-Ni	109.0(5)
Ni-N(4)-C(10)	108.8(6)	Ni-N(2)-C(12)	109.5(5)
C(9)-N(4)-C(10)	111.2(7)	C(13)-N(2)-C(12)	111.9(7)
N(4)-C(10)-C(11)	113.5(8)	N(2)-C(12)-C(11)	112.8(8)
C(10)-C(11)-C(12)	115.1(8)		
C(3)-C(2)-C(19)	121.5(8)		
N(3)-Ni-N(1)	95.3(3)		
N(4)-Ni-N(2)	91.6(3)		

* Entries are arranged with chemically equivalent bond lengths/angles on the same lines.

(*b*) *Metal Complexes* $[ML^1]X_n$ *and* $[ML^2]X_n$ ($M = Co^{III}, Ni^{II}$, *or* Cu^{II}; $X = ClO_4, BF_4$, Cl, *or* NCS; $n = 1$ *or* 2).—Stoicheiometric quantities of metal(II) salt and the ligand were heated together in MeOH. The complexes separated in yields of the order of 80% either on cooling or after addition of an appropriate counter ion. The preparation of $[NiL^1][ClO_4]$ (1) is typical. Ligand HL^1 (0.2 g, 0.65 mmol) was added to a solution of $NiCl_2\cdot 6H_2O$ (0.15 g, 0.65 mmol) in refluxing MeOH (75 cm^3). The solution was refluxed for 10 min. Saturated methanolic $Na(ClO_4)$ solution (10 cm^3) was added with stirring. After cooling, the precipitate was collected and gave red-brown plates of $[NiL^1][ClO_4]$ after recrystallisation from acetonitrile.

(*c*) *Oxidative Dehydrogenation of* $[NiL^1][ClO_4]$ (1) *to* (2).—Triethylamine (5 cm^3, excess) was added to a solution of $[NiL^1][ClO_4]$ (1) (0.2 g, 0.43 mmol) in boiling MeOH (100 cm^3) and the solution refluxed for 1 h. The red product was collected and dried *in vacuo* (Found: C, 63.5; H, 4.4; N, 15.3. $C_{19}H_{16}N_4Ni$ requires C, 63.7; H, 4.5; N, 15.6%); yield quantitative.

Table 3. Fractional atomic co-ordinates for $[NiL^1][ClO_4]$

Atom	*x*	*y*	*z*
Ni	0.805 76(11)	−0.088 41(11)	0.576 68(17)
N(1)	0.738 4(6)	0.034 2(6)	0.509 5(9)
N(2)	0.672 5(6)	−0.223 3(7)	0.468 0(10)
N(3)	0.931 6(6)	0.034 4(6)	0.688 0(9)
N(4)	0.868 2(6)	−0.222 0(7)	0.655 3(10)
Cl	0.724 8(2)	0.492 9(2)	0.206 8(4)
C(1)	0.904 0(9)	0.380 0(10)	0.696 2(15)
C(2)	0.875 6(7)	0.231 0(9)	0.653 2(12)
C(3)	0.948 0(7)	0.165 0(8)	0.715 0(11)
C(4)	1.012 1(7)	−0.019 6(8)	0.760 1(12)
C(5)	1.120 0(7)	0.050 6(9)	0.842 4(12)
C(6)	1.187 7(8)	−0.018 1(10)	0.906 8(13)
C(7)	1.153 6(9)	−0.157 4(10)	0.882 8(14)
C(8)	1.050 8(8)	−0.225 6(10)	0.799 7(12)
C(9)	0.980 1(7)	−0.157 8(8)	0.740 6(11)
C(10)	0.786 7(7)	−0.309 3(9)	0.773 8(13)
C(11)	0.671 2(8)	−0.390 2(9)	0.686 0(13)
C(12)	0.606 4(8)	−0.309 0(9)	0.600 5(13)
C(13)	0.603 6(8)	−0.158 1(9)	0.373 3(12)
C(14)	0.510 5(8)	−0.226 7(11)	0.266 1(14)
C(15)	0.447 9(9)	−0.157 8(10)	0.183 8(15)
C(16)	0.479 6(9)	−0.022 8(10)	0.210 5(14)
C(17)	0.573 4(8)	0.047 4(10)	0.315 3(13)
C(18)	0.637 3(8)	−0.021 4(9)	0.400 7(12)
C(19)	0.776 9(7)	0.164 7(9)	0.552 0(12)
O(1)	0.787 4(10)	0.461 2(11)	0.074 7(17)
O(1A)	0.724 0(26)	−0.562 7(27)	0.035 9(38)
O(2)	0.675 0(12)	0.389 6(12)	0.309 3(18)
O(2A)	0.756 9(29)	−0.592 6(30)	0.331 5(43)
O(3)	0.795 2(11)	0.615 2(12)	0.277 9(18)
O(3A)	0.825 6(23)	−0.433 8(28)	0.357 2(38)
O(4)	0.618 7(15)	0.511 8(16)	0.167 5(23)
O(4A)	0.702 8(25)	−0.390 5(27)	0.170 1(37)

Perchlorate oxygens O(1)—O(4) and O(1A)—O(4A) were assigned site occupation factors of 0.75 and 0.25 respectively.

Alternative synthesis of (2). A suspension of (3) in water was prepared following published guidelines.[9] *o*-Phenylenediamine (0.40 g, 3.7 mmol), $[Ni(O_2CMe)_2]\cdot 4H_2O$ (0.44 g, 1.85 mmol), and 1,1,3,3-tetramethoxypropane (0.30 g, 1.85 mmol) were heated under reflux in water (50 cm^3) for 15 min. 3-Ethoxy-2-methylacrolein (0.21 g, 1.85 mmol) was added and the suspension refluxed for 2 h. The red product was collected and dried *in vacuo*. The analysis of this complex is identical to that formed by the first route above, and their i.r. spectra are exactly superimposable.

Crystal Structure Determination.—The *X*-ray data were collected as described previously.[11] The nickel atom was located from a Patterson map and all remaining non-hydrogen atoms from subsequent difference maps. Anisotropic thermal parameters were assigned to the Ni, N, and Cl atoms. The H atoms were not located directly but constrained to lie 0.95 Å from the parent carbon atom in geometrically idealised sites. The methyl group was treated as a rigid body. The perchlorate counter ion was disordered and was refined as two interlocking tetrahedra with the occupancies of equivalent oxygen atoms fixed at 0.75 and 0.25 in each site. In the later stages of refinement the weighting scheme $w = 1/(\sigma^2 F)$ was introduced. Neutral atom scattering factors were used throughout. All computations were performed using SHELX.[12] Tables 2 and 3 give details of selected bond parameters and the atomic co-ordinates for $[NiL^1][ClO_4]$ (1).

Crystal data. (1): $C_{19}H_{21}ClN_4NiO_4$, $M = 463.2$, Triclinic, space group $P\bar{1}$, $a = 12.351(3)$, $b = 10.596(3)$, $c = 7.841(3)$ Å, $\alpha = 91.971(3)$, $\beta = 92.654(3)$, $\gamma = 108.978(3)°$, $U =$

968.01(3) Å^3, $Z = 2$, $D_c = 1.59$ g cm^{-3}, $F(000) = 481.98$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 11.05$ cm^{-1}. $R = 0.064$, $R' = 0.0625$, for 1 715 independent reflections, $F > 6\sigma(F)$.

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