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FULL PAPER

Indole-based mono- and poly-nuclear acyclic chelating systems: syntheses and selected transition metal complexes‡

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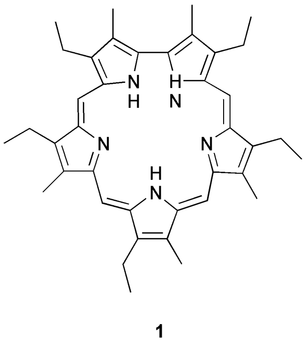
The treatment of 3-(4-chlorophenyl)-4,6-dimethoxyindole with phosphoryl chloride in dimethylformamide generates the regioselective product 3-(4-chlorophenyl)-4,6-dimethoxyindole-7-carbaldehyde. This serves as a valuable ligand precursor and, on reaction with selected di- and tri-amines, yields a number of new acyclic ligands. Treatment of these ligands with selected divalent transition metal acetates in the presence of triethylamine in acetonitrile affords a range of neutral complexes, encompassing both tetrahedral and square-planar metal geometries, of differing nuclearities. In addition to the chemical and physical properties of the ligands and complexes reported, single crystal analyses were employed for geometric analysis in two ligand derivatives: the first, a mononuclear distorted tetrahedral racemic nickel(II) complex; the second, a dinickel heterochiral complex.

Introduction

The porphyrin moiety has been known and extensively studied for decades, and variations on the basic porphyrin unit are to be found in a large proportion of terrestrial organisms. Some time ago Sessler *et al.*[1] reported notable characteristics of what may be viewed as a logical progression of the natural base porphyrin system: an “expanded” 22π pentapyrroloporphyrin called sapphyrin **1**. Since its report in 1966,[2] numerous derivatives of this species have appeared.[3] In the light of this work, indole-based acyclic and macrocyclic chelating systems were envisaged, due to the structural and chemical similarities between pyrrole and indole. Some of these new ligand systems and associated complexes are reported here.



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Tetradentate indole-containing chelate systems have been known for some time,[4] however this work centred around templated Schiff base syntheses. While simplifying the synthetic procedures, such methods usually do not permit studies of the parent free-base ligand due to the rigours of the metal extraction process and susceptibility of the acyclic free bases to imine hydrolysis. Systems of higher denticity can be more laborious to synthesize than tetradentate systems, however they remain synthetic targets for this reason alone, coupled with the often physically and chemically unprecedented characteristics discovered.

Some years ago a general procedure for the synthesis of 3-arylindoles was developed from a method reported by Nordlander *et al.*[5] for the synthesis of indoles *via N*-trifluoroacetyl-2-anilino acetals. These new arylindole derivatives are found to eliminate unwanted reactivity problems, whilst additionally allowing access to new ligand precursors that display differing levels of nucleophilicity at the indole 2 and 7 positions.

The generation of acyclic structures requires that, where two active sites on a precursor exist, activity must be reduced at one position in order to extend maximum synthetic advantage. Strategic positioning of electron-donating methoxy groups on the indole precursor provides nucleophilic activity at the 7 position, whilst modification of the 3-aryl *para* substituent, with respect to electron donating or withdrawing ability, affords a variety of relative levels of nucleophilicity at the indole 2 position. Variation in the geometric arrangements of selected di- and tri-amines thus permitted the production of a range of new indole-containing Schiff base ligands whose transition metal complexes are of differing nuclearities, metal geometries and ligand configurations.

Results and discussion

Ligand precursors and syntheses

Nucleophilically active species react with the Vilsmeier reagent to produce formylated products after basic hydrolysis of the intermediate. For the purposes of the synthesis of acyclic ligands the 3-(4-halogenophenyl)indole derivatives[6] are the most useful due to the electron-withdrawing nature of the *para*-halogeno functionality. The decreased nucleophilic activity at the 2 position of the indole compared with the highly activated 7 position produces a higher yield of 7-formylindole on reaction with the Vilsmeier reagent. No 2-formylindole is observed in formylation reactions except in the case of the highly activ-

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‡ Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format; analytical and physical data for **3**–**10**. See http://www.rsc.org/suppdata/dt/b1/b101350p/

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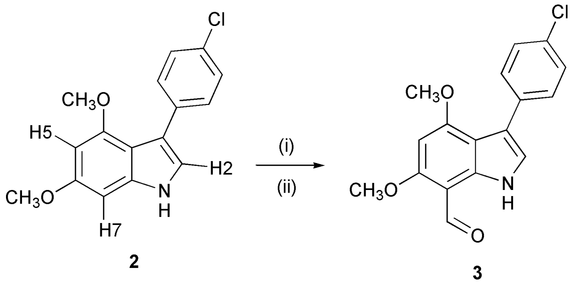
ated 4,6-dimethoxy-3-(4-methoxyphenyl)indole, and then only as a minor product, indicating that in all other instances 2,7 diformylation is preceded by 7 formylation. This hypothesis gains support through recent studies on the corresponding 2-arylindole isomers, where only 7 formylation was observed.[7]

Thus, a chilled solution of 3-(4-chlorophenyl)-4,6-dimethoxyindole **2** in dimethylformamide reacted with a chilled solution of the Vilsmeier reagent to afford 3-(4-chlorophenyl)-4,6-dimethoxyindole-7-carbaldehyde **3** in a yield of 84% (Scheme 1). A ^{1}H NMR investigation of the product indicates the loss of the H7 proton resonance (δ H7 6.45), collapse of the H5 resonance from a doublet in the precursor ($^4J_{H5H7}$ = 1.9 Hz) to a singlet at δ 6.15 and retention of the H2 resonance as a doublet ($^3J_{H2NH}$ = 2.2 Hz). The aldehyde is characterized by a new signal at δ 10.35. All additional spectroscopic and analytical data are in full accord with the proposed structure.



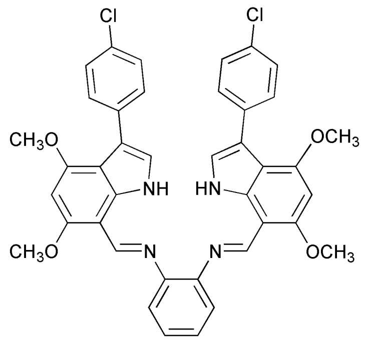
Scheme 1 *Reagents and conditions*: (i) POCl$_3$, DMF, 0 °C; (ii) NaOH, water.

A standard procedure for the syntheses of the target ligands (**4**–**10**) was developed. The combination of starting materials in benzene at reflux under an inert atmosphere in the presence of a trace of *p*-toluenesulfonic acid promoted a steady reaction rate. It is believed that the same electron density increase generated by the methoxy-groups hinders the Schiff base procedure due to the resultant decreased electrophilic character of the formyl carbon. Water removal was effected by the placement of activated, degassed 4A molecular sieves in the catchment arm of a Dean–Stark apparatus. The methods of product isolation varied according to the physical characteristics and hydrolytic susceptibilities of the compounds, and are commented on individually where necessary.

Mononuclear systems

Complexes of 4. Treatment of **4** with nickel(II), cobalt(II), copper(II) and palladium(II) acetates afforded the neutral, highly insoluble square-planar complexes **4a**–**d** respectively (Scheme 2). The nickel(II) and palladium(II) complexes are characterised by molecular ions in their FAB mass spectra corresponding to the respective M + 1 Cl$^{35/35}$ mass units; the cobalt(II) complex displays a 90% relative intensity peak. The FAB mass spectrum of the copper(II) complex displays only mass signals for the demetallated complex, a phenomenon which has been observed in the FAB mass spectra of similar systems and is commented upon elsewhere.[8]

The cobalt, copper and palladium complexes are all brown, whilst the nickel complex is red. The ^{1}H NMR spectrum of the nickel(II) complex mirrors that of the C_2 symmetric free-base ligand with small field shifts (*ca.* 0.1–0.2 ppm) for all signals. Of



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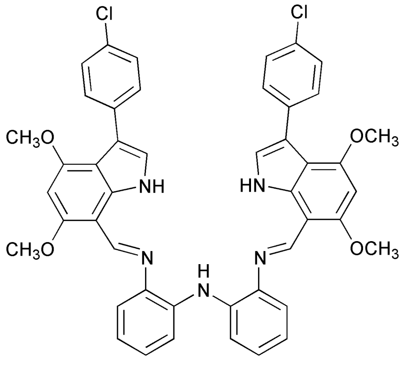

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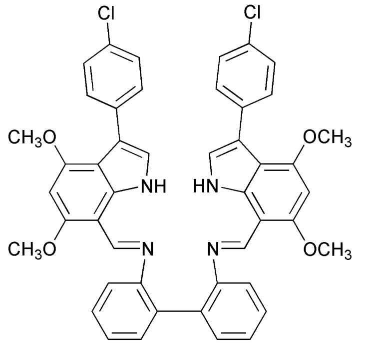

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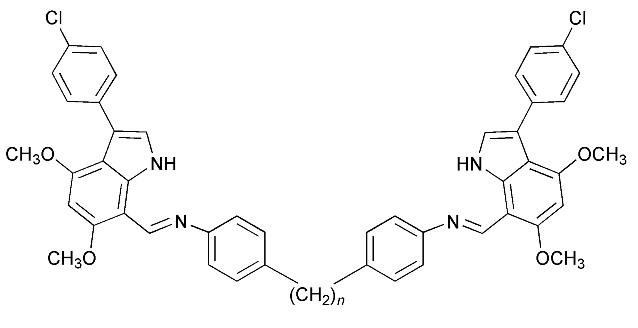
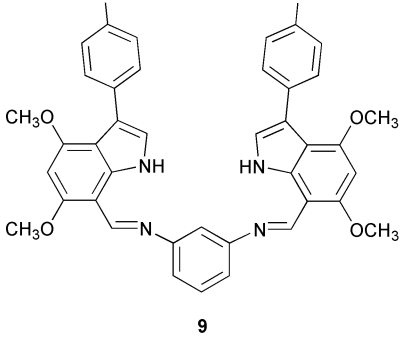


7 $n = 1$
8 $n = 2$



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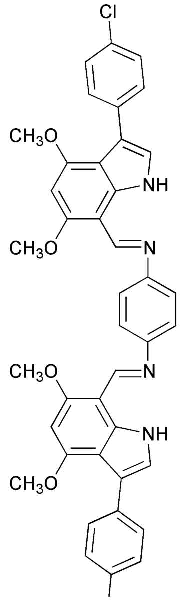

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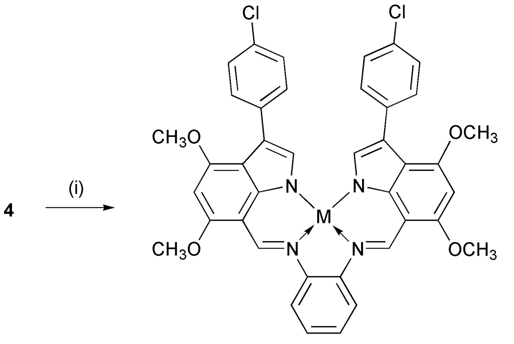
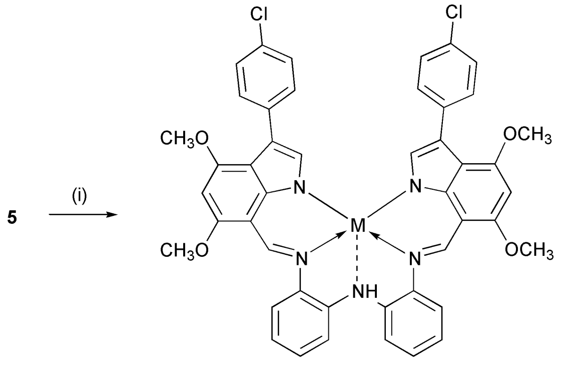


4a–d
M = Ni, Co, Cu, Pd

Scheme 2 *Reagents and conditions*: (i) $M(OAc)_2{\cdot}nH_2O$, CH_3CN, Et_3N, Δ.

note is the slight upfield shift from δ 9.15 to 8.91 observed for the imine proton resonance on chelation, presumably due to the proximity of the shielding metal orbitals. The downfield shift of 0.36 ppm of the H2 proton resonance is indicative of a net loss of electron density in the indole moiety due to the presence of the metal and formation of covalent N–M bonds. The absence of evidence for axial ligands, particularly in the NMR (**4a** and **4d**) and IR spectra, strongly suggests that all complexes are square-planar neutral species.

Complexes of 5. Reaction of ligand **5** with cobalt(II), copper(II), and zinc(II) acetates affords complexes **5b**–**d** respectively that are all mononuclear and, based on physical and spectroscopic data, their collective metal geometries are postulated as distorted tetrahedral, with possible supporting chelation from the bridging amino lone pair (Scheme 3). The cobalt(II) complex yields a weak molecular ion under mass spectral analysis. In the case of the copper(II) complex only demetallation fragments are observed, as for **4c**, whilst the zinc(II) complex gave a strong molecular ion. A demetallation peak was also observed for all complexes excepting that of cobalt(II).



5b–d
M = Co, Cu, Zn

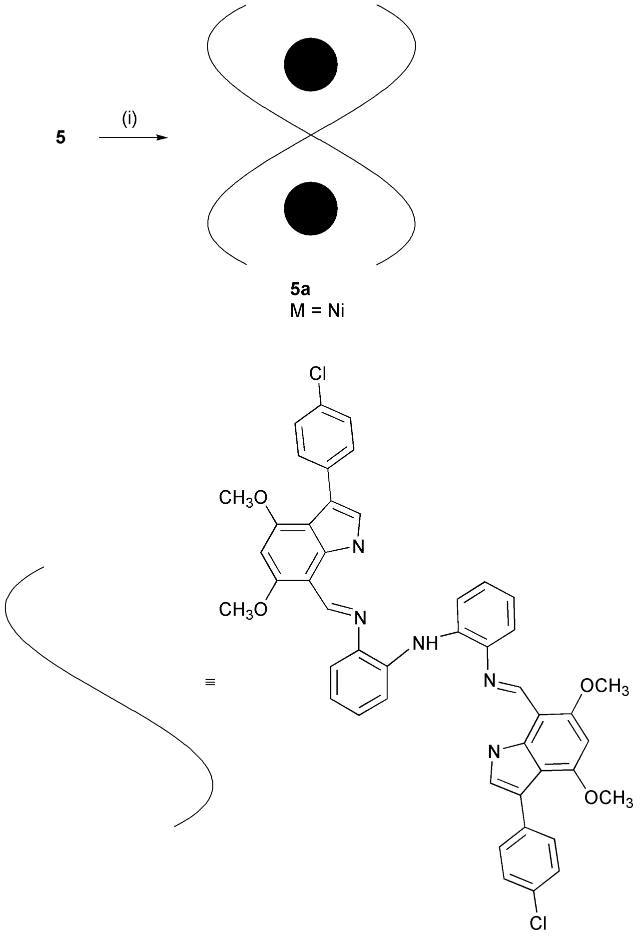
Scheme 3 *Reagents and conditions*: as in Scheme 2.

No absorption from the bridging NH was observed in the IR spectra of any of the complexes, possibly due to its low intensity, or as a result of weak dative interaction with the metal centre: the proximity of the amino lone pair to the metal centre would suggest the latter to be likely. The zinc(II) complex displays a ^1H NMR spectrum that closely parallels that of the free-base ligand, as anticipated, with the obvious omission of the indole NH resonance.

The complexes decomposed on attempted recrystallization. This thermal instability is suggestive of an imperfect coordination sphere with respect to the requirements of the metal centre. Ligand **5** failed to coordinate palladium(II), presumably because it cannot easily support a square-planar chelation mode.

Treatment of **5** with nickel(II) acetate in acetonitrile at reflux produced an immediate change from the orange of the free-base ligand to red-brown. Isolation of **5a** followed by spectroscopic investigation indicated a complex that is structurally different from those previously discussed. An NH absorption is visible in the IR spectrum at 3354 cm^{-1}, indicative of a non-coordinating bridging amino group, in contrast to complexes **5b**–**d**. Additionally, the fingerprint region of the spectrum differs notably from those for the previous complexes. The ^1H NMR spectrum indicates the presence of paramagnetic (and therefore non-planar) nickel atoms, with a large array of resonances observed.

A FAB mass spectral analysis gave an ion at *m*/*z* 1701 and a smaller peak at *m*/*z* 851, corresponding to Ni_2L_2 and NiL respectively. Modelling studies with tetrahedral metal centres suggest that the dimer is unlikely to adopt a pseudo-linear "*meso*" structure, where the two ligands are parallel and approximately linear, even though examples of such complexes appear in the literature.[9] In the absence of a solid-state analysis we thus tentatively suggest that the Ni_2L_2 complex adopts a less sterically demanding helical structure (Scheme 4).

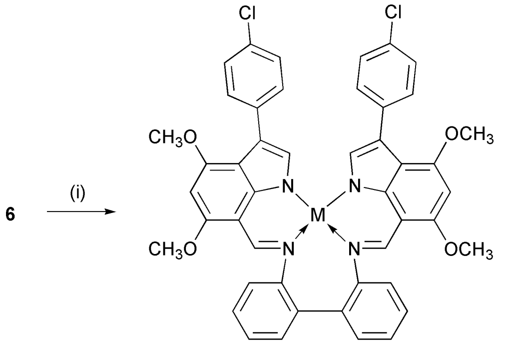


5a
M = Ni

Scheme 4 *Reagents and conditions*: (i) $Ni(OAc)_2{\cdot}4H_2O$, CH_3CN, Et_3N, Δ.

A MALDI (matrix-assisted laser-desorption ionization)-TOF analysis of **5a** gave peaks of 45 and 25% relative intensities corresponding to Ni_2L_2 and NiL_2 respectively, and peaks of 100 and 90% relative intensities corresponding to NiL and L respectively. It is unclear whether fragmentation of a dinuclear complex is being seen, or whether a mixture of mononuclear and dinuclear complexes is present. The large number of resonances observed in the ^1H NMR spectrum of the complex suggests the latter to be correct, although it is uncertain if these species retain structural integrity in solution.

Complexes of 6. Extended heating of **6** in acetonitrile was required to effect metal complexation, affording complexes **6a-d** (Scheme 5). The spectral data are in accord with the proposed structures. The zinc(II) complex **6d** gave a molecular ion under MALDI conditions yet showed demetallation under FAB ionization.



6a–d
M = Ni, Co, Cu, Zn

Scheme 5 *Reagents and conditions*: as in Scheme 2.

The ^{1}H NMR spectrum of the zinc complex is unremarkable whilst that of the nickel complex shows resonances over a field of some 100 ppm (signals are observed from δ −10 to 90) and is indicative of a paramagnetic complex. Interestingly, the resonance linewidths were found not to be excessively large, as is the case with many paramagnetic NMR spectra.[9] The observed massive field shifts and loss of polarization due to the presence of the paramagnetic metal centre meant that few routine proton assignments could be made. The integral ratios in combination with a ^{1}H–^{1}H correlation permitted peak assignments to be made with some degree of accuracy. The extreme downfield broad singlet at δ 90.00 is tentatively assigned as the resonance of the imine proton with H2, being spatially closest to the metal centre, unobserved.

The vast solubility difference between the free-base ligand and its complexes is noteworthy. The 2,2′-biphenyl linkage necessarily enforces great torsional deformation in the chelate ring about the annular linkage. The free-base ligand is able to alleviate these steric interactions by adopting a more linear conformation, which presumably reduces solubility. The stepwise coordination of metal ions would then produce a more compact and easily solvated structure, resulting in the observed greater solubility of the complex.

The crystal and molecular structures of **6a** were determined (Tables 1 and 3). The complex crystallises in the monoclinic space group $P2_1/c$. The nickel atom lies in a distorted tetrahedral environment with bond angles of 98.8, 91.9, 109.6 and 93.6°. Coordination of a tetrahedral metal centre by an unsymmetrical bis-bidentate ligand affords a chiral complex; the Δ enantiomer is depicted in Fig. 1. The nickel–indole nitrogen bond distances are Ni–N1 1.930(5) Å and Ni–N3 1.922(5) Å, whilst the Ni–imine nitrogen bond distances are Ni–N2 1.984(6) Å and Ni–N4 1.994(5) Å, illustrating the stronger bonds to the electron-rich indole unit. The structure also shows that the Ni–imine hydrogen distance is approximately 3.9 Å and the Ni–indole H2 distance is 3.2 Å, reinforcing the proton NMR assignment.

In contrast to the red planar complex **4a** the tetrahedral complex **6a** is almost black, reflecting the significant geometrically enforced chromophoric differences and the qualitative manner in which the geometry of the metal centre in these neutral indole complexes can be deduced.

Table 1 Selected bond lengths (Å), angles and torsional angles (°) for compound **6a**·CHCl$_3$

Ni–N1	1.930(5)	N1–Ni–N2	93.6(2)
Ni–N2	1.984(6)	N1–Ni–N3	109.6(2)
Ni–N3	1.922(5)	N1–Ni–N4	140.6(2)
Ni–N4	1.994(5)	N2–Ni–N3	127.5(2)
N1–C1	1.376(8)	N2–Ni–N4	98.8(2)
N1–C8	1.361(8)	N3–Ni–N4	91.9(2)
N2–C17	1.324(8)	Ni–N1–C1	129.7(4)
N2–C18	1.435(8)	Ni–N1–C8	124.9(5)
		C17–N2–C18	115.0(6)
		C18–C23–C46–C41	−64.8(9)

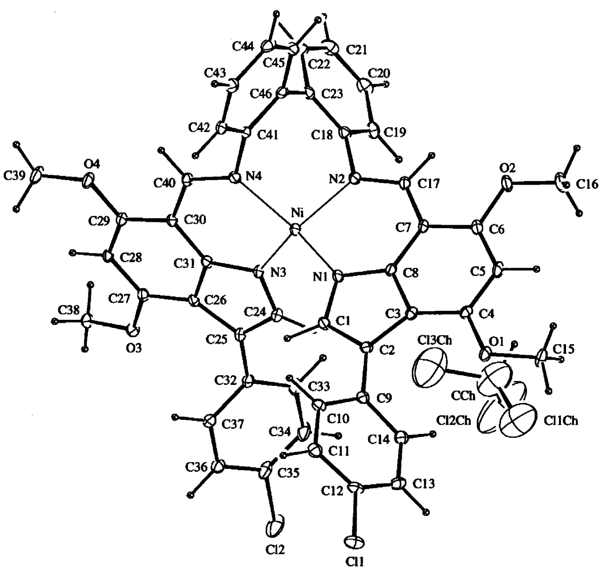


Fig. 1 Thermal ellipsoid diagram of **6a**·CHCl$_3$. Ellipsoids indicate 10% probability levels.

Dinuclear systems

The synthesis of dinuclear complexes requires certain basic conditions to be met. The ligands must possess at least two coordinating domains, and the linkage between these domains must display some degree of flexibility so as to facilitate the coordination of two metal atoms by one ligand. Additionally, the ligand should not be linear or capable of forming mononuclear complexes. Two commercially available diamines were seen to fulfil these requirements in choosing a ligand precursor: 4,4′-methylenedianiline and 4,4′-ethylenedianiline. One important feature that led to the selection of these two particular diamines is that the nature of the molecular fulcrum in each case is based on a tetrahedron, which should favour formation of a “bent” conformation. Additionally, the complexes of the more flexible ethane-linked ligand would provide valuable comparisons with those obtained from the methylene-linked complexes, given the difference in ligand bite angle produced in each case.

Complexes of 7. In each case it was decided to treat the ligand with nickel(II) acetate, because of the information provided by the ^{1}H NMR spectra of the complexes, even in the case of a paramagnetic complex. Additionally, in the case of **7**, cobalt(II) was included for examination due to its larger ionic radius when compared with nickel(II), and the lack of electronic preference for square-planar coordination that the d^8 metal ion possesses.

Ligand **7** was treated with nickel(II) acetate tetrahydrate to yield **7a**. The ^{1}H NMR spectrum of the complex (Fig. 2) indicates the presence of tetrahedral nickel, in that the resonances are observed over a field range of some 50 ppm. Only ten resonances are observed, indicating that the complex possesses C_2 or higher symmetry. As with **6a** a single upfield resonance is

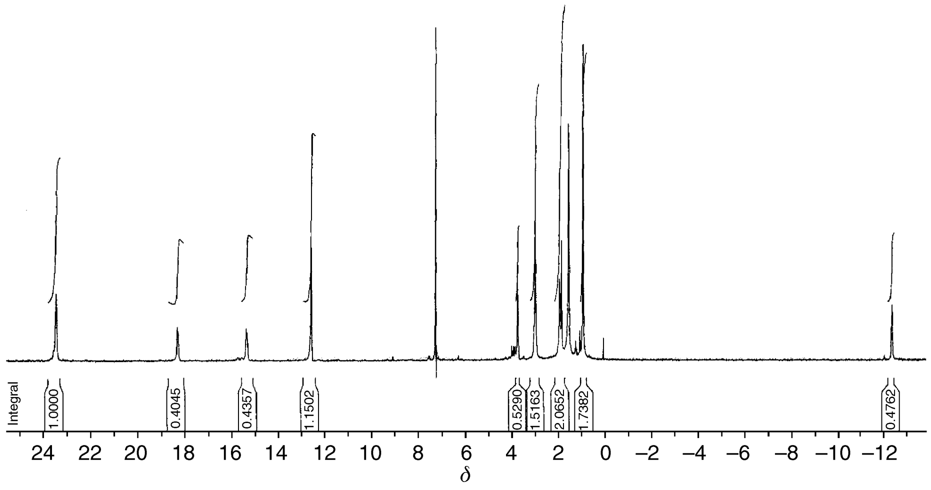
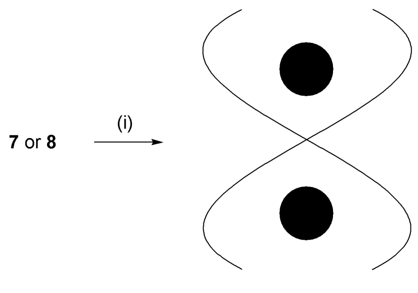


Fig. 2 ^{1}H NMR spectrum (299.95 MHz; [^{2}H]chloroform) of **7a**, illustrating the presence of a symmetrical dimer with paramagnetic tetrahedral nickel metal centres.

observed near δ −10. No IR absorption is observed in the range of 3600–3200 cm^{-1}, indicating coordination saturation. A MALDI-TOF mass spectral analysis displays a 15% relative intensity peak at *m*/*z* 1701, corresponding to the target Ni_2L_2 mass unit.

The mass ion at *m*/*z* 1701 clearly indicates the presence of a 2 : 2 complex. Modelling studies suggest that a linear dinuclear complex is disfavoured in preference for a double helix (Scheme 6). The formation of helical species with such a ligand is not without precedent given that a similar ligand, using the same coordinating domain spacer, forms a dinuclear triple helicate in the presence of nickel(II):[10] presumably **7** does not form a species of identical stoichiometry as the literature example due to the bis-anionic coordination domains.



7a,b M = Ni, Co
8a,b M = Ni, Zn

Scheme 6 *Reagents and conditions*: as in Scheme 2.

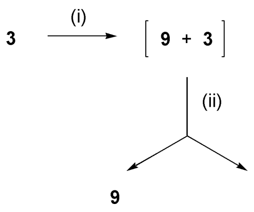
Peaks corresponding to the Co_2L_2 mass unit were also obtained for the complex **7b**.

Complexes of 8. Complex **8a** (Scheme 6) shows no NH-assignable absorption in the IR spectrum. Mass spectral demetallation was observed as in the case of **4c** and **6a**, again indicating possible weak coordination of the metal. The paramagnetic ^{1}H NMR spectrum of **8a** indicates tetrahedral nickel atoms. Only ten resonances are observed, suggesting C_2 or higher symmetry, which strongly implies a dimer.

Zinc complex **8b** also displayed no NH absorptions in its IR spectrum and gave a Zn_2L_2 peak at *m*/*z* 1741. The breakdown pattern of **8b** is similar to that observed for the complexes of **7**, indicating that the tertiary structures of the two groups of complexes are potentially quite similar. Unfortunately, **8b** was found to be too insoluble for ^{1}H NMR characterization.

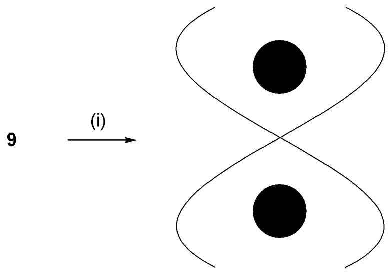
Since the formation of a dinuclear *meso* species is strongly disfavoured and in consideration of the literature precedent for helicate formation in ligands employing this spacer,[10] it is suggested that the preferred conformation of these complexes is that of a double helix.

Reaction of 3 with 1,3-diaminobenzene. The synthesis of **9** was expected to produce a ligand whose coordination field was too large to form mononuclear complexes with the first-row transition metals employed in this study, thus forcing the ligand to form di- or poly-nuclear species. 1,3-Diaminobenzene was treated with **3** but product formation was slow and incomplete. Unchanged **3** was removed by the addition of small amounts of 2,2′-diaminobiphenyl (*ca.* 10 mg) to the reaction mixture, producing highly insoluble **6**. After the solvent was removed under reduced pressure, the solid residue was boiled in chloroform and filtered hot to separate the two ligands (Scheme 7). Spectroscopic and physical data for **9** are in full accord with the proposed structure.



Scheme 7 *Reagents and conditions*: (i) 1,3-diaminobenzene, C_6H_6, Δ, N_2; (ii) 2,2′-diaminobiphenyl, $CHCl_3$, Δ.

Complexes of 9. Complexes **9a–c** were produced according to the standard procedure (Scheme 8). A palladium(II) complex could not be formed, indicating the preference of **9** for tetrahedral chelation. MALDI-TOF mass spectral analyses curiously indicated the formation of mononuclear complexes,



9a–c M = Ni, Cu, Co

Scheme 8 *Reagents and conditions*: as in Scheme 2.

Table 2 Selected bond lengths (Å) and angles (°) for compound **9a**·7DMF

Ni1–N1	1.910(5)	N1–Ni1–N2	92.5(2)
Ni1–N2	1.998(5)	N1–Ni1–N3	118.0(2)
Ni1–N3	1.922(5)	N1–Ni1–N4	127.1(2)
Ni1–N4	1.996(5)	N2–Ni1–N3	121.7(2)
N1–C1	1.376(6)	N2–Ni1–N4	107.6(2)
N1–C4	1.367(6)	N3–Ni1–N4	92.3(2)
N2–C9	1.320(6)	Ni1–N2–C9	126.5(4)
N2–C35	1.422(6)	Ni1–N2–C35	115.8(3)
Ni···Ni	7.211(4)	Ni1–N3–C18	129.1(4)
		Ni1–N3–C21	125.3(4)

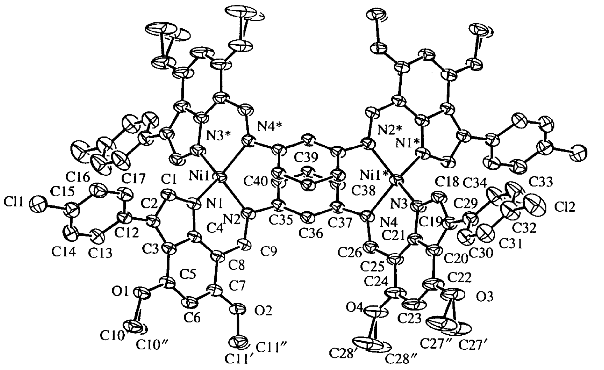


Fig. 3 Thermal ellipsoid diagram of **9a**·7DMF with labelling of selected atoms. Asterisks indicate atoms that have been generated by the crystallographic symmetry operation ($-x$, $1-y$, $1-z$). Both locations of each disordered atom are shown. Ellipsoids indicate 30% probability levels. Hydrogen atoms and solvent molecules have been omitted for clarity.

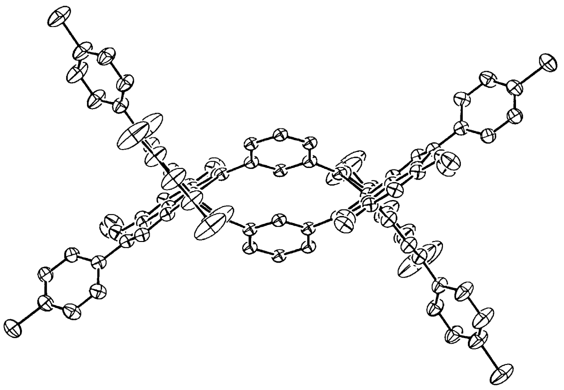


Fig. 4 Thermal ellipsoid diagram of **9a**·7DMF. Both locations of each disordered atom are shown. Ellipsoids indicate 30% probability levels. Hydrogen atoms and solvent molecules have been omitted for clarity.

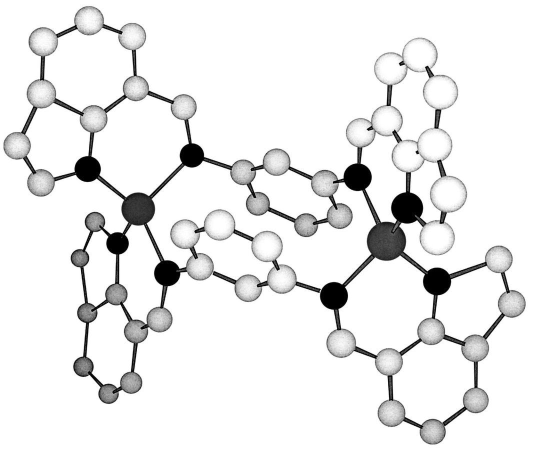


Fig. 5 Partial molecular structure of **9a**·7DMF, showing the *meso*-like disposition of the ligands about the Ni–Ni axis. Peripheral atoms and solvent molecules have been omitted for clarity.

with demetallation peaks observed for **9b** and **9c**. Complex **9a** is black, again indicative of a tetrahedral metal geometry.

Complexes **9a–c** were crystallised from dimethylformamide as rectangular blocks. Removal of these crystals from the mother liquor induced immediate decomposition. In order for a structural analysis to be undertaken, a suitable crystal of **9a** was drawn into a glass capillary onto glass fibres so that the crystal remained in contact with the mother liquor. The sealed assembly was used for data collection.

The complex **9a** (Figs. 3 and 4) exists in the solid state as a dimer, with a centre of inversion coincident with a crystallographic inversion centre of $P\bar{1}$; bond lengths and angles are given in Table 2 and crystallographic data appear in Table 3. Nickel-to-indole and -imine bond lengths compare favourably with those of the mononuclear species **6a**; the Ni···Ni distance is 7.211(4) Å. One half of the dimer shows distinctly more thermal motion than the other and the C atoms of the four methoxy groups of the crystallographic asymmetric unit were regarded as 1 : 1 disordered. There are 7 solvent molecules per unit cell, one of them disordered about 1/2,0,0 and all have large thermal motion, explaining the lack of crystal stability on removal from the mother liquor. Refinement used the constrained refinement program RAELS 96[11] so as to allow anisotropic thermal parameters to be defined by rigid body parameterizations. This allowed just 270 independent variables adequately to refine the structure down to $R(F) = 0.074$ for the 4299 reflections with $I > 3\sigma(I)$ used in the refinement. The Ni was refined as an isolated anisotropic atom but the remaining atoms were described using local coordinates defined relative to orthonormal axial systems.[12]

The dimer has inherent $2/m$ symmetry with the inversion centre being exact: the distances hold this symmetry relationship well. The nickel coordination is distorted tetrahedral, with bond angles of 92.5, 92.3, 118.0 and 107.6°, with the last two angles showing the only significant departure from the inherent symmetry relationships between angles in the dimer.

The adoption of tetrahedral geometry by the metal is believed to be a means of reducing the aryl H2–metal interaction, to such an extent that the electronic preference of nickel(II) for square-planar geometry is overcome. It appears that, on coordination of the metal ion, the interaction between the aryl H2 and the metal atom (in addition to the large size of the coordination sphere) is sufficient to discourage planar coordination but does not preclude the formation of a dimeric complex with two tetrahedral metal centres. Since the ligand is achiral the resulting complex is a *meso* species and is therefore also achiral, with metal centres of opposing chirality.

It is particularly noteworthy that the system does not adopt the more common helical coordination mode observed for ligands of this type.[13] In such cases the ligands are seen to wrap themselves about the metal–metal axis,[9,13] however **9a** forms a complex whereby each ligand remains essentially on one side only of the metal–metal axis (Fig. 5). The exception to this is the central region where π-stacking necessitates the proximity of the aryl spacers.

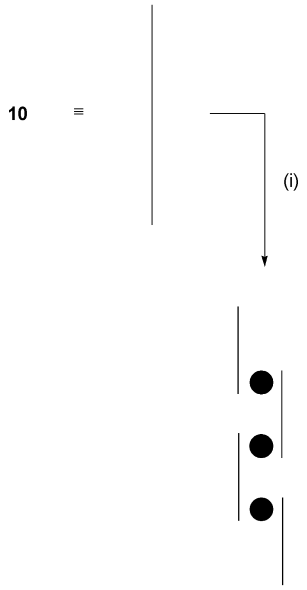
On the basis of these observations it is presumed that the cobalt and copper complexes **9b** and **9c** are also dinuclear, given the similarities in physical data with those of **9a**.

Complexes of 10. Ligand **10** was treated with nickel(II) acetate tetrahydrate (Scheme 9). A yield calculation of 99% was based on a hypothetical monomeric complex **10a**.

The ^{1}H NMR spectrum of the complex corresponds to that of a paramagnetic sample with many resonances, indicating the presence of at least one tetrahedral nickel atom. The low ratio of NH-(normally a medium-strong absorption)-to-fingerprint IR absorptions indicates that either the sample is contaminated with unchanged ligand, or that only a relatively small amount

Table 3 Crystallographic data for complexes **6a**·$CHCl_3$ and **9a**·7DMF

	6a·$CHCl_3$	**9a**·7DMF
Formula	$C_{46}H_{34}Cl_2N_4NiO_4 \cdot CHCl_3$	$C_{80}H_{60}Cl_4N_8Ni_2O_8 \cdot 7C_3H_7NO$
M	955.8	2032.28
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	13.342(3)	12.952(12)
b/Å	20.470(5)	14.602(12)
c/Å	20.763(5)	15.286(13)
α/°	—	70.36(6)
β/°	128.417(8)	71.35(6)
γ/°	—	85.15(7)
u/Å^3	4443(2)	2579(4)
Z	4	1
μ(Mo-K$_\alpha$)/cm^{-1}	7.88	5.37
T/K	294	273.2
No. of reflections		
(total)	5784	9135
(unique)	3641	4299
R_{int}	0.021	0.028
R, R_w	0.066, 0.101	0.074, 0.101



10a,b M = Ni, Co

Scheme 9 *Reagents and conditions*: as in Scheme 2.

of uncoordinated indole remains corresponding to the uncoordinated terminal indoles of a polymer. A MALDI-TOF mass spectral analysis of the sample afforded only demetallated complex peaks. These data and the lack of discrete chelate masses in the mass spectrum suggest that **10a** is polymeric.

Cobalt analogue **10b** displays two imine absorptions at 1598 and 1539 cm^{-1}, corresponding to uncoordinated and coordinated stretching modes respectively. The fingerprint region of the spectrum strongly resembled that of the nickel complex, but was vastly different from that of the free-base ligand. A MALDI-TOF mass spectral analysis produced only peaks corresponding to a demetallated complex, as in the case of **10a**, however laser desorption of the sample with no matrix afforded peaks at m/z 2256 and 1506, which correspond approximately to the Co_2L_3 and Co_2L_2 structures respectively. It is therefore considered that **10b** is also polymeric.

No reaction occurred between **10** and palladium acetate, suggesting that the metal geometries in **10a** and **10b** are tetrahedral.

The products **10a** and **10b** were studied by transmission electron microscopy. The images obtained from the nickel complex **10a** illustrate that it exists as rod-like structures. In addition, these rods appear to congregate in clusters, perhaps due to van der Waals forces or hydrogen-bonding interactions. Complex **10b** exhibits an amorphous structure and neither **10a** nor **10b** gave a diffraction pattern under an X-ray beam, indicating the absence of crystalline material.

Conclusion

A range of new indole-containing acyclic ligands has been produced and their coordinating abilities probed by employing first-row transition metals of varying ionic size and electronic geometrical preferences. The metal geometries were established qualitatively, by consideration of the extremely characteristic colours of the nickel(II) complexes and ^1H NMR data, and quantitatively in two cases *via* crystallographic analyses. In each of the solid state analyses the metal was found to possess a distorted tetrahedral disposition. The complex **9a** was found to exist as a heterochiral dimer in the solid state. MALDI-TOF mass spectral analyses proved particularly useful for accumulating evidence for the formation of dinuclear species in the absence of structural characterizations.

Experimental

Melting points are uncorrected. Microanalyses were performed by Dr H. P. Pham of the University of New South Wales. ^1H and ^{13}C NMR spectra were obtained in the designated solvents on a Bruker AC300F (300 MHz) spectrometer, variable temperature ^1H NMR spectra using a Bruker AM500 (500 MHz) spectrometer. Data are given as the chemical shift measured in parts per million (ppm), proton count, multiplicity, observed coupling constant (J) in Hertz (Hz). Multiplicities are reported as singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q) and multiplet (m). ^{13}C NMR chemical shifts are reported in ppm downfield from TMS (δ); the carbon count and identifiable carbons are given. Transmission electron microscopy was performed by Ms Vera Piegerova on a JEOC STEM 2000FX. Infrared spectra were recorded as KBr discs on a Mattson Sirius 100 FTIR spectrometer. Nujol mulls were recorded on a Perkin-Elmer 298 or 580B spectrometer. Ultraviolet-visible spectra were obtained in acetonitrile on a Hitachi UV-3200 spectrophotometer. CI mass spectra were recorded on a Kratos MS902 or MS840 instrument, EI mass spectra on an AEI MS 12 mass spectrometer at 70 eV ionizing potential and 8000 V accelerating voltage with an ion source temperature of 210 °C, FAB mass spectra on a VG Biotech Quattro triple quadrupole spectrometer or a VG Autospec (Mark 1) spectrometer in EBE configuration, using p-nitrobenzoic acid–dichloromethane 50 : 50 as a matrix and MALDI-TOF mass spectra on a

Finnigan MAT Lasermat 2000. The *m*/*z* values of the principal ion peaks are reported together with their percentage intensities relative to the base peak (where possible). Flash chromatography was carried out using Merck silica gel 7730 60GF$_{254}$.

Anhydrous tetrahydrofuran (THF) was distilled from potassium and benzophenone; dimethylformamide (DMF) was dried over calcium hydride then distilled under reduced pressure onto activated 4A molecular sieves; chloroform ($CHCl_3$) was distilled from phosphorus pentaoxide, diethyl ether from sodium and benzophenone. 3-(4-Chlorophenyl)-4,6-dimethoxyindole **2** was prepared according to the literature procedure.[6] 1,2-, 1,3-, 1,4-Diaminobenzene, 4,4′-methylenedianiline and 4,4′-ethylenedianiline were obtained commercially and purified before use. 2,2′-Diaminobiphenyl was prepared from the corresponding commercially available dinitro species according to the literature procedure.[14] 2,2′-Diaminodiphenylamine was prepared according to the literature procedure.[14]

Preparations

General method for Schiff bases. The stoichiometric amounts of the appropriate aldehyde and amine were placed in a suitably sized multi-necked round bottom flask. A Dean–Stark apparatus was affixed between flask and condenser, the catchment arm of which contained activated, degassed 4A molecular sieves. The solutions were heated at reflux under a dinitrogen atmosphere and the reaction was monitored by TLC. On completion of the reaction, the products were filtered off where solids were obtained, or the solvent was removed and the product obtained by chromatographic purification where possible.

General method for complexes. The ligand was suspended or dissolved in acetonitrile near reflux and anhydrous triethylamine (3 drops) followed by the metal acetate was added. Heating of the mixture at reflux was continued for the specified duration, after which the mixture was filtered and the solid washed with acetonitrile then anhydrous diethyl ether, air dried and collected.

3-(4-Chlorophenyl)-4,6-dimethoxyindole-7-carbaldehyde 3. To a stirred solution of 3-(4-chlorophenyl)-4,6-dimethoxyindole **2** (5.00 g, 17.4 mmol) in anhydrous dimethylformamide at −15 °C was added dropwise an ice cold solution of phosphoryl chloride (4.00 g, 26.1 mmol) in dimethylformamide (3 mL). The mixture was stirred at this temperature for 1 h, then allowed to come to room temperature. Ice–water (10 mL) was added and the mixture stirred vigorously for 1 h, then made alkaline (pH 9) with 10% sodium hydroxide solution and stirred vigorously for 4 h. The mixture was then neutralized with 2 M HCl solution and extracted with dichloromethane (3 × 100 mL), the organic layer collected, dried ($MgSO_4$) and the solvent removed under reduced pressure. The resulting solid was purified by column chromatography (CH_2Cl_2–n-hexane 50 : 50 eluent) and the uppermost band collected and crystallized from dichloromethane–n-hexane to afford compound **3** as yellow crystals (4.6 g, 84%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) 3.89 and 3.96 (6 H, s, OCH_3), 6.15 (1 H, s, H5), 7.04 (1 H, d, J_{H2NH} 2.2, H2), 7.29 and 7.45 (4 H, d, *J* 8.5 Hz, chlorophenyl), 10.35 (1 H, s, CHO), 10.49 (1 H, br s, NH); δ_C(299.95 MHz; solvent and standard [^{2}H]chloroform) 55.44 and 56.43 (2 C, OCH_3), 86.88, 121.85, 127.70 and 130.66 (6 C, aryl CH), 104.52, 110.03, 117.73, 131.90, 133.94 and 137.77 (8 C, aryl C), 188.37 (1 C, CHO); *m*/*z* (EI) 316 (M + 1, 20%), 315 (M^+, 100), 300 (20), 265 (50), 229 (10), 78 (40), 43 (60), 32 (100), 28(100).

1,2-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzene 4. The aldehyde **3** (0.610 g, 1.93 mmol) and 1,2-diaminobenzene (0.100 g, 0.942 mmol) were treated according to the general procedure. After 72 h of heating at reflux a precipitate was observed and the mixture was cooled, filtered and the residue recrystallized from CH_2Cl_2 to afford the ligand as orange-yellow needles (0.298 g, 45%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) 3.87 and 3.91 (12 H, s, OCH_3), 6.22 (2 H, s, H5), 6.51 (2 H, s, H2), 7.23 and 7.4 (8 H, d, *J* 9.0 Hz, chlorophenyl), 7.26 and 7.30 (4 H, m, aryl), 9.15 (2 H, s, CH=N), 11.61 (2 H, br s, NH); too insoluble for δ_C; *m*/*z* (FAB) 707 (M + 1, $Cl^{37/37}$, 20%), 706 (M^+, $Cl^{37/37}$, 35), 705 (M + 1, $Cl^{35/37}$, 75), 704 (M^+, $Cl^{35/37}$, 60), 703 (M + 1, $Cl^{35/35}$, 100), 702 (M^+, $Cl^{35/35}$, 25).

{1,2-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzenato(2−)}nickel(II) 4a. This compound was prepared according to the general method using ligand **4** (0.100 g, 0.142 mmol) dissolved in the minimum amount of acetonitrile at reflux and nickel(II) acetate tetrahydrate (0.037 g, 0.15 mmol), prompting an immediate change from yellow-orange to a vivid red-brown, The mixture was heated at reflux for 1 h, then allowed to cool to room temperature, chilled and filtered. The product was washed with acetonitrile followed by anhydrous diethyl ether, affording the complex as red-brown microcrystals (0.102 g, 95%). δ_H(299.95 MHz; solvent [^{2}H]-chloroform; standard $SiMe_4$) 3.96 and 4.04 (12 H, s, OCH_3), 6.16 (2 H, s, H5), 6.87 (2 H, s, H2), 7.17 (6 H, m, chlorophenyl + 2 H aryl), 7.47 (4 H, d, *J* 8.5, chlorophenyl), 7.70 (2 H, dd, *J* 6.0, 3.0 Hz, aryl), 8.91 (2 H, s, CH=N); too insoluble for δ_C; *m*/*z* (FAB) 763 (M, $Cl^{37/37}$, 20%), 762 (M + 1, $Cl^{35/37}$, 55), 761 (M^+, $Cl^{35/37}$, 75), 760 (M + 1, $Cl^{35/35}$,100), 759 (M^+, $Cl^{35/35}$,70), 758 (M − 1, $Cl^{35/35}$, 75), 746 (50), 726 (40), 721 (20), 705 (20).

{1,2-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzenato(2−)}cobalt(II) 4b. This compound was prepared according to the general method using ligand **4** (0.100 g, 0.142 mmol) and cobalt(II) acetate tetrahydrate (0.037 g, 0.15 mmol) and obtained as red-brown microcrystals (0.101 g, 94%). *m*/*z* (FAB) 764 (M^+, $Cl^{37/37}$, 10%), 763 (M + 1, $Cl^{35/37}$, 30), 762 (M^+, $Cl^{35/37}$, 60), 761 (M + 1, $Cl^{35/35}$, 90), 760 (M^+, $Cl^{35/35}$, 85), 759 (M − 1, $Cl^{35/35}$, 100), 746 (15), 726 (5), 703 (15).

{1,2-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzenato(2−)}copper(II) 4c. This compound was prepared according to the general method using ligand **4** (0.100 g, 0.142 mmol) and copper(II) acetate monohydrate (0.0297 g, 0.149 mmol) under a dinitrogen atmosphere and obtained as brown microcrystals (0.071 g, 65%). *m*/*z* (FAB) 706 (demetallated complex, L + 1, 55%).

{1,2-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzenato(2−)}palladium(II) 4d. This compound was prepared according to the general method using ligand **4** (0.100 g, 0.142 mmol) and palladium(II) acetate (0.034 g, 0.15 mmol) and obtained as brown microcrystals (0.098 g, 86%). *m*/*z* (FAB) 812 (M + 1, $Cl^{37/37}$, 30%), 811 (M^+, $Cl^{37/37}$, 45), 810 (M + 1, $Cl^{35/37}$, 70), 809 (M^+, $Cl^{35/37}$, 75), 808 (M + 1, $Cl^{35/35}$, 100), 807 (M^+, $Cl^{35/35}$, 80), 806 (M − 1, $Cl^{35/35}$, 85), 805 (50), 804 (20), 793 (8).

2,2′-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]diphenylamine 5. A mixture of **3** (1.23 g, 3.88 mmol) and 2,2′-diaminodiphenylamine (0.368 g, 1.85 mmol) was heated according to the standard procedure. The crude solid was collected by filtration, purified by thin-layer chromatography (CH_2Cl_2–n-hexane 70 : 30 eluent) and recrystallized from dichloromethane–n-hexane to afford compound **5** as orange-yellow crystals (1.25 g, 85%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) 3.78 and 3.81 (12 H, s, OCH_3), 6.03 (2 H, s, H5), 6.38 (2 H, d, J_{NHH2} 2.3, H2), 6.96 (2 H, t, *J* 7.4, aryl), 7.17 (3 H, m, aryl), 7.25 and 7.33 (4 H, d, *J* 8.6, chlorophenyl), 7.47 (1 H, t, *J* 7.4, aryl), 7.61 (2 H, t, *J* 7.4 Hz, aryl), 7.63 (1 H, br s, NH), 9.07 (2 H, s, CH=N), 10.92 (2 H, br s, NH); δ_C(299.95 MHz; solvent and standard [^{2}H]chloroform) 55.12 and 56.58 (4 C, OCH_3), 87.67, 114.98, 118.51, 120.56, 121.72, 126.18, 127.44 and 130.48 (20 C, aryl CH), 102.62, 109.92, 116.90, 131.22, 134.40, 136.67, 137.17, 141.83, 158.29 and 159.43 (10 C, aryl C), 156.20 (2 C, CH=N); *m*/*z* (EI) 799 (M + 1, $\mathrm{Cl}^{37/37}$, 1%), 798 (M^+, $\mathrm{Cl}^{37/37}$, 2), 797 (M + 1, $\mathrm{Cl}^{35/37}$, 3), 796 (M^+, $\mathrm{Cl}^{35/37}$, 4), 795 (M + 1, $\mathrm{Cl}^{35/35}$, 5), 794 (M^+, $\mathrm{Cl}^{35/35}$, 4), 779 (3), 613 (1), 586 (1), 507 (1), 494 (2), 460 (3), 413 (1), 391 (3), 361 (1), 349 (3), 329 (5), 307 (100), 289 (60), 273 (5), 220 (5).

{Bis[2,2′-bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]diphenylaminato(2−)]}dinickel(II) 5a. This compound was prepared according to the general method using ligand **5** (0.0300 g, 0.0378 mmol) dissolved in the minimum amount of acetonitrile at reflux (20 mL) and nickel(II) acetate tetrahydrate (0.0141 g, 0.0566 mmol). The complex was obtained as deep red crystals (0.016 g, 50%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) paramagnetic and unassignable; *m*/*z* (FAB) 1707 (M^+, $\mathrm{Cl}^{35/37/37/37}$, 10%), 1706 (M + 1, $\mathrm{Cl}^{35/35/37/37}$, 30), 1705 ($M^+$, $\mathrm{Cl}^{35/35/37/37}$, 40), 1704 (M + 1, $\mathrm{Cl}^{35/35/35/37}$, 50), 1703 ($M^+$, $\mathrm{Cl}^{35/35/35/37}$, 40), 1702 (M + 1, $\mathrm{Cl}^{35/35/35/35}$, 90), 1701 ($M^+$, $\mathrm{Cl}^{35/35/35/35}$, 100), 856 (M + 1, NiL, $\mathrm{Cl}^{37/37}$, 5%), 855 (M^+, $\mathrm{Cl}^{37/37}$, 10), 854 (M + 1, $\mathrm{Cl}^{35/37}$, 12), 853 (M^+, $\mathrm{Cl}^{35/37}$, 25), 852 (M + 1, $\mathrm{Cl}^{35/35}$, 30), 851 (M^+, $\mathrm{Cl}^{35/35}$, 50), 550 (20), 507 (15). *m*/*z* (MALDI-TOF) 1699 (Ni_2L_2, 50%), 1642 (NiL_2, 30), 851 (NiL, 100), 795 (L, 90).

{2,2′-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]diphenylaminato(2−)}cobalt(II) 5b. This compound was prepared according to the general method using ligand **5** (0.0300 g, 0.0378 mmol) dissolved in the minimum amount of acetonitrile at reflux (20 mL) and cobalt(II) acetate tetrahydrate (0.0095 g, 0.038 mmol) and obtained as deep brown crystals (0.010 g, 31%). *m*/*z* (EI, 300 °C) 855 (M^+, $\mathrm{Cl}^{37/37}$, 1%), 854 (M + 1, $\mathrm{Cl}^{35/37}$, 2), 853 (M^+, $\mathrm{Cl}^{35/37}$, 3), 852 (M + 1, $\mathrm{Cl}^{35/35}$, 5), 851 (M^+, $\mathrm{Cl}^{35/35}$, 5), 567 (20), 553 (30).

{2,2′-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]diphenylaminato(2−)}copper(II) 5c. This compound was prepared according to the general method using ligand **5** (0.0300 g, 0.0378 mmol) dissolved in the minimum amount of acetonitrile at reflux (20 mL) and copper(II) acetate monohydrate (0.0150 g, 0.0566 mmol), and obtained as deep red-brown crystals (0.015 g, 46%). *m*/*z* (FAB) (decomplexation fragments observed only) 798 (M^+, $\mathrm{Cl}^{37/37}$, 1%), 797 (M + 1, $\mathrm{Cl}^{35/37}$, 2), 796 (M^+, $\mathrm{Cl}^{35/37}$, 2), 795 (M + 1, $\mathrm{Cl}^{35/35}$, 3), 794 (M^+, $\mathrm{Cl}^{35/35}$, 3), 557 (3), 513 (4), 469 (3), 453 (4), 437 (2), 409 (3), 393 (5), 375 (3), 349 (4), 331 (7), 313 (4), 287 (6), 271 (30), 245 (80), 227 (100), 209 (80).

2,2′-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]diphenylaminato(2−)}zinc(II) 5d. This compound was prepared according to the general method using ligand **5** (0.0700 g, 0.0881 mmol) dissolved in the minimum amount of acetonitrile at reflux (20 mL) and zinc(II) acetate monohydrate (0.0213 g, 0.0969 mmol) and was obtained as bright orange microcrystals (0.057 g, 75%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) 3.78 and 3.88 (12 H, s, OCH_3), 5.79 (1 H, s, NH bridging), 6.64 (2 H, s, H5), 6.75 and 6.88 (6 H, m, aryl), 6.91 (2 H, s, H2), 7.15 (8 H, s, chlorophenyl), 7.20 (2 H, s, aryl), 8.64 (2 H, s, CH=N); too insoluble for δ_C; *m*/*z* (MALDI-TOF) 859 (M + 2, 85%), 795 (demetallated complex, 55).

2,2′-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]biphenyl 6. The aldehyde **3** (0.688 g, 2.18 mmol) and 2,2′-diaminobiphenyl (0.200 g, 1.09 mmol) were treated according to the general procedure. After 1 h a yellow precipitate was observed to form. After 48 h the mixture was allowed to cool to room temperature then filtered and washed with anhydrous diethyl ether, affording yellow microcrystals (0.808 g, 95%). Sample too insoluble for δ_H or δ_C; *m*/*z* (FAB) 783 (M + 1, $\mathrm{Cl}^{37/37}$, 25%), 782 (M^+, $\mathrm{Cl}^{37/37}$, 50), 781 (M + 1, $\mathrm{Cl}^{35/37}$, 95), 780 (M^+, $\mathrm{Cl}^{35/37}$, 70), 779 (M + 1, $\mathrm{Cl}^{35/35}$, 100), 778 (M^+, $\mathrm{Cl}^{35/35}$, 20).

{2,2′-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]biphenylato(2−)}nickel(II) 6a. This compound was prepared according to the general method using ligand **6** (0.100 g, 0.128 mmol) and nickel(II) acetate tetrahydrate (0.032 g, 0.13 mmol). After 10 min the yellow suspension was observed to take on a brown colouration. The mixture was heated at reflux for 1.5 h, after which little solid remained. The solution was allowed to come to room temperature then chilled and the resulting suspension filtered. The crude product was recrystallized from ethyl acetate (100 mL) to afford the complex as brown crystals (0.080 g, 75%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) −9.25 (2 H, s, H5), −6.21 and 19.89 (4 H, s, aryl), −5.57 (2 H, br s, aryl), 1.28 and 3.69 (12 H, s, OCH_3), 2.84 (4 H, d, *J* 7.3, chlorophenyl), 11.69 (4 H, d, *J* 7.6, chlorophenyl), 17.01 (2 H, d, *J* 5.6 Hz, aryl), 90.00 (2 H, br s, CH=N), H2 unobserved; *m*/*z* (FAB) (demetallation fragments observed only) 783 (M + 1, $\mathrm{Cl}^{37/37}$, 20%), 782 (M^+, $\mathrm{Cl}^{37/37}$, 40), 781 (M + 1, $\mathrm{Cl}^{35/37}$, 80), 780 (M^+, $\mathrm{Cl}^{35/37}$, 65), 779 (M + 1, $\mathrm{Cl}^{35/35}$, 100), 778 (M^+, $\mathrm{Cl}^{35/35}$, 20).

{2,2′-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]biphenylato(2−)}cobalt(II) 6b. This compound was prepared according to the general method using ligand **6** (0.100 g, 0.128 mmol) and cobalt(II) acetate tetrahydrate (0.034 g, 0.14 mmol), and obtained as orange-brown crystals (0.092 g, 86%). *m*/*z* (FAB) 840 (M + 1, $\mathrm{Cl}^{37/37}$, 1%), 839 (M^+, $\mathrm{Cl}^{37/37}$, 2), 838 (M + 1, $\mathrm{Cl}^{35/37}$, 3), 837 (M^+, $\mathrm{Cl}^{35/37}$, 5), 836 (M + 1, $\mathrm{Cl}^{35/35}$, 4), 835 (M^+, $\mathrm{Cl}^{35/35}$, 5).

{2,2′-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]biphenylato(2−)}copper(II) 6c. This compound was prepared according to the general method using the ligand **6** (0.100 g, 0.128 mmol) and copper(II) acetate monohydrate (0.027 g, 0.14 mmol), and obtained as orange-brown crystals (0.086 g, 80%). *m*/*z* (FAB) 845 (M + 1, $\mathrm{Cl}^{37/37}$, 15%), 844 (M^+, $\mathrm{Cl}^{37/37}$, 35), 843 (M + 1, $\mathrm{Cl}^{35/37}$, 60), 842 (M^+, $\mathrm{Cl}^{35/37}$, 80), 841 (M + 1, $\mathrm{Cl}^{35/35}$, 100), 840 (M^+, $\mathrm{Cl}^{35/35}$, 70).

{2,2′-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]biphenylato(2−)}zinc(II) 6d. This compound was prepared according to the general method using ligand **6** (0.050 g, 0.064 mmol) and zinc(II) acetate dihydrate (0.014 g, 0.067 mmol), with the mixture heated at reflux for 12 h. The yellow solution was filtered hot through a bed of Celite under vacuum then all solvent was removed. The solid was boiled in methanol to afford a yellow suspension, which was filtered and dried to afford compound **6d** as yellow microcrystals (0.047 g, 87%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) 3.906 and 3.910 (12 H, s, OCH_3), 6.11 (2 H, s, H5), 7.11 (3 H, s, aryl), 7.13 (2 H, s, H2), 7.23 and 7.34 (9 H, m, aryl), 7.47 (4 H, d, *J* 8.5 Hz, chlorophenyl), 8.92 (2 H, s, CH=N); δ_C(299.95 MHz; solvent and standard [^{2}H]chloroform) 55.29 and 56.47 (4 C, OCH_3), 85.54 (2 C, C5), 122.46, 126.44, 127.54, 129.46, 130.31, 131.71 and 134.63 (16 C, aryl CH), 101.79, 111.98, 117.18, 130.40, 134.28, 135.63, 144.94, 149.82, 161.64 and 161.89 (20 C, aryl C), 162.92 (2 C, CH=N); *m*/*z* (MALDI-TOF) 858 (M + 1, $\mathrm{Cl}^{35/35}$, 20%).

4,4′-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]diphenylmethane 7. The 7-formylindole **3** (0.637 g, 2.02 mmol) and 4,4′-methylenedianiline (0.200 g, 1.01 mmol) were treated according to the standard procedure. A yellow precipitate was observed after 24 h. Reflux was continued for 4 days, then the mixture was cooled and filtered. The product was found to undergo hydrolysis on silica, so treatment with charcoal in chloroform followed by recrystallization from dichloromethane–n-hexane afforded the ligand as yellow crystals (0.521 g, 65%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) 3.91 and 3.98 (1 2H, s, OCH_3), 4.06 (2 H, s, CH_2), 6.28 (2 H, s, H5), 7.14 (2 H, s, H2), 7.24 (8 H, d, *J* 1.8, aryl), 7.34 and 7.56 (8 H, dt, *J* 8.5, 2.0 Hz, chlorophenyl), 9.09 (2 H, s, CH=N), 11.40 (2 H, br s, NH); δ_C(299.95 MHz; solvent and standard [^{2}H]chloroform) 41.04 (1 C, CH_2), 55.29 and 56.77 (4 C, OCH_3), 87.69, 121.30, 121.72, 127.76, 129.68 and 130.72 (20 C, aryl CH), 102.44, 110.25, 117.49, 131.61, 134.53, 137.60, 138.37, 150.96, 158.33 and 159.38 (20 C, aryl C), 155.89 (2 C, CH=N); *m/z* (FAB) 798 (M + 1, $Cl^{37/37}$, 10%), 797 (M^+, $Cl^{37/37}$, 25), 796 (M + 1, $Cl^{35/37}$, 45), 795 (M^+, $Cl^{35/37}$, 80), 794 (M + 1, $Cl^{35/35}$, 75), 793 (M^+, $Cl^{35/35}$, 100), 792 (M − 1, $Cl^{35/35}$, 30), 781 (15), 766 (10), 746 (25), 726 (20), 697 (8), 663 (7), 629 (50), 613 (60).

Bis{4,4′-bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]diphenylmethanato(2−)}dinickel(II) 7a. This compound was prepared according to the general method using ligand **7** (0.150 g, 0.189 mmol) and nickel(II) acetate tetrahydrate (0.0470 g, 0.189 mmol), resulting in an immediate change from yellow to brown, and the mixture was heated at reflux for 8 h. The mixture was filtered warm and the solid washed with acetonitrile then anhydrous diethyl ether and dried to afford compound **7a** as brown microcrystals (0.137 g, 85%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) (paramagnetic compound, total assignment not possible) −12.74 (4 H, s, H2 or H5), 0.93 and 3.67 (24 H, s, OCH_3), 2.00 (4 H, s, CH_2), 2.26 (16 H, br s, aryl), 13.03 and 24.44 (16 H, s, chlorophenyl), 33.81 (4 H, s, H2 or H5); *m/z* (MALDI-TOF) 1701 (Ni_2L_2, 15%), 1641 (NiL_2, 10), 794 (L, 55).

Bis{4,4′-bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]diphenylmethanato(2−)}dicobalt(II) 7b. This compound was prepared according to the general method using ligand **7** (0.150 g, 0.189 mmol) and cobalt(II) acetate tetrahydrate (0.0490 g, 0.198 mmol) and obtained as red-brown microcrystals (0.129 g, 80%). *m/z* (MALDI-TOF) 1703 (Co_2L_2, 60%), 1645 (CoL_2, 35), 795 (L + 1, 70).

4,4′-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]diphenylethane 8. The 7-formylindole **3** (0.595 g, 1.88 mmol) and 4,4′-ethylenedianiline (0.200 g, 9.42 mmol) were treated according to the standard procedure. The resulting yellow solid was purified by charcoal treatment in chloroform (due to its observed hydrolysis on silica) followed by recrystallization from chloroform to afford the ligand as yellow crystals (1.14 g, 75%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) 2.98 (4 H, s, CH_2), 3.92 and 3.99 (12 H, s, OCH_3), 6.29 (2 H, s, H5), 7.16 (2 H, s, H2), 7.23 (8 H, s, aryl), 7.34 and 7.56 (8 H, dt, *J* 8.4, 1.8 Hz, chlorophenyl), 9.10 (2 H, s, CH=N), 11.42 (2 H, br s, NH); δ_C(299.95 MHz; solvent and standard [^{2}H]chloroform) 37.62 (2 C, CH_2), 55.31 and 56.81 (4 C, OCH_3), 87.70, 121.12, 121.70, 127.75, 129.25 and 130.70 (20 C, aryl CH), 102.48, 110.26, 117.49, 131.62, 134.55, 137.62, 138.85, 150.75, 158.30 and 159.35 (20 C, aryl C), 155.73 (2 C, CH=N); *m/z* (FAB) 812 (M + 1, $Cl^{37/37}$, 10%), 811 (M^+, $Cl^{37/37}$, 25), 810 (M + 1, $Cl^{35/37}$, 45), 809 (M^+, $Cl^{35/37}$, 80), 808 (M + 1, $Cl^{35/35}$, 75), 807 (M^+, $Cl^{35/35}$, 100), 806 (M − 1, 30), 793 (15), 781 (10), 746 (15), 721 (10), 705 (7), 643 (45), 629 (7), 613 (30).

Bis{4,4′-bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]diphenylethanato(2−)}dinickel(II) 8a. This compound was prepared according to the general method using ligand **8** (0.0800 g, 0.0990 mmol) and nickel(II) acetate tetrahydrate (0.0271 g, 0.0109 mmol), resulting in an immediate change from yellow to brown, and the mixture was heated at reflux for 3 h. The complex was obtained as brown microcrystals (0.067 g, 78%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) (paramagnetic compound, total assignment not possible) −12.35 (4 H, s), 0.94 (8 H, s), 1.87 and 1.94 (24 H, s), 2.98 (8 H, s), 3.75 (4 H, s), 12.58 (8 H, s), 15.3 and 18.3 (8 H, d, *J* 9.2 Hz, chlorophenyl), 23.45 (8 H, s); *m/z* (MALDI-TOF) 808 (demetallated complex, 100%).

Bis{4,4-bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]diphenylethanato(2−)}dizinc(II) 8b. This compound was prepared according to the general method using ligand **8** (0.080 g, 0.099 mmol) and zinc(II) acetate monohydrate (0.0239 g, 0.0109 mmol), and obtained as orange microcrystals (0.071 g, 82%), too insoluble for δ_H and δ_C; *m/z* (MALDI-TOF) 1741 (Zn_2L_2, 10%), 1678 (ZnL_2, 8), 809 (demetallated complex, 100).

1,3-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzene 9. 1,3-Diaminobenzene (0.171 g, 1.58 mmol) and **3** (1.00 g, 3.17 mmol) were treated according to the general procedure. The reaction was monitored by TLC and observed not to go to completion. A small aliquot was taken, the solvent removed and the crude solid examined by ^{1}H NMR, indicating contamination by **3** and the diamine. Small amounts of 2,2′-diaminobiphenyl (*ca.* 10 mg) were added and the reaction was continued and monitored by TLC until all **3** was observed to have reacted. The mixture was cooled and the solvent removed under reduced pressure. The residue was boiled in chloroform and the suspension filtered hot. The solid material was collected and shown to be identical to a genuine sample of **6**. The filtrate was collected and the solvent removed. The crude solid was crystallized form dichloromethane–n-hexane to afford compound **9** as orange needles (0.256 g, 23%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) 3.93 and 4.00 (12 H, s, OCH_3), 6.29 (2 H, s, H5), 7.13 (2 H, dd, *J* 7.9, 2.0, aryl H4,6), 7.17 (2 H, s, H2), 7.19 (1 H, d, *J* 2.0, aryl H2), 7.34 and 7.55 (8 H, dt, *J* 8.5, 1.8, chlorophenyl), 7.42 (1 H, t, *J* 8.0 Hz, aryl H5), 9.16 (2H, s, CH=N), 11.41 (2 H, br s, NH); δ_C(299.95 MHz; solvent and standard [^{2}H]chloroform) 55.30 and 56.76 (4 C, OCH_3), 87.65 (2 C, C5), 127.77 and 130.72 (8 C, chlorophenyl CH), 110.25, 113.98, 118.08 and 121.73 (6 C, aryl CH), 102.38, 117.54, 129.69, 131.62, 134.48 and 137.62 (12 C, aryl C), 153.81 (2 C, *C*N=CH), 156.41 (2 C, CH=N), 158.51 and 159.55 (4 C, *C*OCH_3); *m/z* (MALDI-TOF) 704 (M + 1, $Cl^{35/35}$, 100%).

Bis{1,3-bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzenato(2−)}dinickel(II) 9a. This compound was prepared according to the general method using ligand **9** (0.050 g, 0.071 mmol) and nickel(II) acetate tetrahydrate (0.0195 g, 0.0782 mmol), resulting in an immediate change from yellow to brown. The mixture was heated at reflux for 2 h, filtered warm and the solid washed with acetonitrile followed by anhydrous diethyl ether and dried to afford compound **9a** as brown microcrystals (0.041 g, 76%). δ_H(299.95 MHz; solvent [^{2}H]dimethylformamide; standard $SiMe_4$) multiple unassignable resonances; δ_C(299.95 MHz; solvent and standard [^{2}H]dimethylformamide) multiple unassignable resonances; *m/z* (MALDI-TOF) 781 (M + Na, 55%).

Bis{1,3-bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzenato(2−)}dicobalt(II) 9b. This compound was prepared according to the general method using ligand **9** (0.050 g, 0.071 mmol) and cobalt acetate tetrahydrate (0.0195 g, 0.0782 mmol), and obtained as red-brown microcrystals (0.046 g, 85%). *m/z* (MALDI-TOF) 782 (M + Na, 100%), 705 (M − Co, 80).

Bis{1,3-bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzenato(2−)}dicopper(II) 9c. This compound was prepared according to the general method using ligand **9** (0.050 g, 0.071 mmol) and copper(II) acetate monohydrate

(0.0209 g, 0.0853 mmol), and obtained as brown microcrystals (0.044 g, 82%). *m*/*z* (MALDI-TOF) 766 (M + 1, 40%), 705 (M − Cu, 100).

1,4-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzene 10. The aldehyde **3** (0.600 g, 1.90 mmol) and 1,4-diaminobenzene (0.100 g, 0.942 mmol) were treated according to the standard procedure with the use of anhydrous toluene as solvent. After 20 h a yellow precipitate was observed, and after further heating for 96 h the mixture was cooled, filtered and the solid washed with diethyl ether. Charcoal treatment of a chloroform solution (2 L) of the crude product followed by solvent removal, filtration and washing with dichloromethane afforded compound **10** as yellow microcrystals (0.411 g, 62%). δ_H(299.95 MHz; solvent [^{2}H]chloroform; standard $SiMe_4$) 3.93 and 4.01 (12 H, s, OCH_3), 6.30 (2 H, s, H5), 6.91 (2 H, s, H2), 7.15–7.35 (12 H, m, aryl H), 9.14 (2 H, s, CH=N), indole NH unobserved; too insoluble for δ_C; *m*/*z* (FAB) 707 (M + 1, $Cl^{37/37}$, 20%), 706 (M, $Cl^{37/37}$, 35), 705 (M + 1, $Cl^{35/37}$, 75), 704 (M, $Cl^{35/37}$, 60), 703 (M + 1, $Cl^{35/35}$, 100), 702 (M, $Cl^{35/35}$, 25).

{1,4-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzenato(2−)}nickel(II) polymer 10a. This compound was prepared according to the general method using ligand **10** (0.100 g, 0.142 mmol) and nickel(II) acetate tetrahydrate (0.0354 g, 0.142 mmol), resulting in an immediate change from yellow to brown, and the mixture was heated at reflux for 8 h. It was filtered warm and the product washed with acetonitrile then anhydrous diethyl ether and dried to afford a brown solid (0.108 g, 100%). δ_H(299.95 MHz; solvent [^{2}H]-chloroform; standard $SiMe_4$) (paramagnetic compound) −10.97 (s), 0.9–4.5 (m), 12.5–13 (m), 18.8–20.1 (br s), 121.0 (br s); *m*/*z* (MALDI-TOF) 720 (30%), 704 (demetallated complex, 40).

{1,4-Bis[3-(4-chlorophenyl)-4,6-dimethoxyindol-7-ylmethyleneamino]benzenato(2−)}cobalt(II) polymer 10b. This compound was prepared according to the general method using ligand **10** (0.100 g, 0.142 mmol) and cobalt(II) acetate tetrahydrate (0.0354 g, 0.142 mmol), and afforded a red-brown solid (0.103 g, 96%). *m*/*z* (MALDI-TOF) 735 (25%), 718 (45), 704 (demetallated complex, 95); *m*/*z* (MALDI-TOF) no matrix 2256 (20%), 1506 (40), 719 (55), 705 (55).

Crystallography

The data were collected on Nonius CAD-4 (**6a**·$CHCl_3$) or Philips PW1100/20 (**9a**·7DMF) instruments. Crystallographic data are summarized in Table 3.

CCDC reference numbers 159043 and 159044.

See http://www.rsc.org/suppdata/dt/b1/b101350p/ for crystallographic data in CIF or other electronic format.

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