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Synthesis and Characterization of Some Macrocylic Complexes Incorporating Indole and 2,2'-Bipyridine or 1,10-Phenanthroline

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ABSTRACT: Complexes of anionic pentadentate macrocyclic ligands by the template condensation of bis(hydrazino)2,2'-bipyridine or 1,10-phenanthroline with an indoledialdehyde have been synthesized. The new Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) macrocyclic complexes have been characterized by analytical and spectroscopic techniques and by conductivity and magnetic susceptibility measurements.

Keywords: Macrocyclic complexes; Transition metals; Magnetic susceptibility measurements.

تكوين ودراسة خصائص بعض المعقدات الخماسية الحلقة من الأندول و 2,'2- ثنائي البيريدين أو10,1- الفينانثرولين

محمد خان ، نوال الراسبية وادوين كونيستابل

ملخص: تم تكوين معقدات من المترابطات الخماسية الحلقة المشتقة من تفاعلات التكاثف بين ثنائي هايدرازين 2,'2-ثنائي البيريدين أو 10,1- الفينانثرولين مع أندول ألديهايد. وتم تكوين معقدات جديدة خماسية الحلقة من المنجنيز(II) و الحديد (II) والكوبالت (II) والنيكل (II) وأخيرا الزنك (II). كما تمت دراسة خصائصها عن طريق التحليل التقني والتوصيل الكهربائي والخصائص المغناطيسية.

كلمات مفتاحية: معقدات خماسية الحلقة، العناصر الانتقالية، قياس القابلية المغناطيسية.

1. Introduction

In the past six decades macrocyclic ligands and complexes incorporating an enormous variety of functional groups have been prepared and investigated [1, 2]. There has been particular interest in macrocyclic systems incorporating heterocyclic subunits, which may provide donor atoms for a metal ion and also act as rigid structure formers. Metal complexes of polydentate macrocyclic ligands have also attracted interest because of their potential for providing molecules capable of mimicking various aspects of biological systems [3].

In the early to late 1980s, Lewis and Constable reported a variety of macrocyclic systems incorporating 1,10-phenanthroline, 2,2'-bipyridine [4-29], 2,2':6',2''-terpyridine [30-34] and 2,2'-biquinoline [35] moieties into the cyclic structure. More recently, the group of Constable and Housecroft have designed a series of dinuclear macrocyclic ligands containing multiple bipyridines or terpyridines coordinated to Fe(II) [36]. Metal-directed self-assembly of macrocyclic compounds bearing terpyridine pendants bound to Fe(II), Ru(II) and Pt(II) [37-43] have also been investigated.

As an extension to these studies, in this paper, we investigate the utility of indoledialdehyde for the preparation of macrocycles. We describe the preparation and characterization of cyclic hydrazones formed from a 2,7-diformylindole. We also investigate their coordination chemistry with some d-block metal ions such as Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II).

2. Experimental

2.1 General details

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were pre-dried and distilled before use by standard procedures. All chemicals were obtained from Sigma Aldrich and used as received. Infra-red spectra were recorded in compressed KBr pellets on a Perkin-Elmer 1710 FT spectrophotometer.

^{I}H NMR spectra were recorded on a Brüker WM-250 or a AM-400 spectrometer. Mass spectra were recorded on a Kratos MS 890 mass spectrometer by the fast atom bombardment (FAB) technique. Microanalyses were performed in the University Chemical Laboratory, University of Cambridge. Cyclic voltammograms were conducted in a Princeton Applied Research Electrochemistry System, model 170. A Pt wire sealed in glass was the auxiliary electrode with a second Pt wire serving as the working electrode, and a $Ag/AgNO_3$ as the reference electrode. Measurements were made in acetonitrile solution with 0.1 M $[^{t-}Bu_4N]BF_4]$ as the base electrolyte. A CDM 210 conductivity meter was used to measure conductivity in nitromethane solution. Magnetic susceptibility measurements were done using a Sherwood Scientific MKI Model Gouy Balance. The bis(hydrazines) $\mathbf{L^2}$-$\mathbf{L^7}$ [4-29] and 2,7-indoledildehyde (**HL)** [45-49] were prepared as reported in the literature.

2.2 Preparation of complexes

Preparation of $[Ni\mathbf{L^8}][BF_4]$

A solution of $Ni(OAc)_2.4H_2O$ (0.100 g, 0.4 mmol) in MeOH (15 cm^3) was added to a solution of **HL** (0.100 g, 0.4 mmol) in MeOH (15 am^3) at 70 °C under an inert atmosphere. After 5 minutes, a solution of $\mathbf{L^2}$ in MeOH (15 cm^3) was added, and the mixture heated to reflux for 5 h, during which period it turned orange-yellow. The solution was concentrated *in vacuo* to one third volume and $Na[BF_4]$ (0.04 g) added to the hot solution. After cooling, an orange microcrystalline solid was precipitated. Recrystallisation from MeOH followed by drying *in vacuo* gave $[NiL^8][BF_4]$ as an orange solid (65% yield). Anal. Found: C, 49.1; H, 4.3; N, 14.9. Calc. for $C_{27}H_{28}N_7O_4NiBF_4$: C, 49.1; H, 4.2; N, 14.9%. FAB-MS: *m/z* 574.65 $\{Ni\mathbf{L^8}\}^+$. I.R. (KBr), 1590m, 1530m, 1260m, 1225w, 1180w, 1151s, 1090br, 960br, 844s, 830m, 750s cm^{-1}.

Preparation of $[Co\mathbf{L^8}(H_2O)][PF_6]$

A solution of $Co(OAc)_2.4H_2O$ (0.100 g, 0.4 mmol) in MeOH (15 cm^3) was added to a solution of **HL** (0.100 g, 0.4 mmol) in MeOH (15 cm^3) at 70 °C under an inert atmosphere. After 5 minutes, a solution of $\mathbf{L^2}$ in MeOH (15 cm^3) and triethylamine (0.041 g, 0.4 mmol) were added, and the mixture heated to reflux for 5 h, during which period it turned orange-yellow. The solution was concentrated in *vacuo* to one third volume and $[NH_4][PF_6]$ (0.064 g) was added to the hot solution. After cooling $[Co\mathbf{L^8}(H_2O)][PF_6]$ was precipitated as an orange microcrystalline solid (65% yield). Anal. Found: C, 44.2; H, 4.1; N, 13.8. Calc. for $C_{27}H_{30}N_7O_4CoPF_6$: C, 44.0; H, 4.1; N, 13.3%. FAB-MS: *m/z* 574.02 $\{Co\mathbf{L^8}\}^+$. I.R. (KBr), 3500br, 1660w, 1593s, 1262m, 1230w, 1174w, 1148s, 1094br, 960br, 849s cm^{-1}.

All other complexes were prepared in similar manners. Analytical data for the complexes are presented in Table 1. The ^{1}H NMR data of the Zn(II) complexes are presented in Table 2.

Table 1. Analytical data for metal macrocyclic complexes.

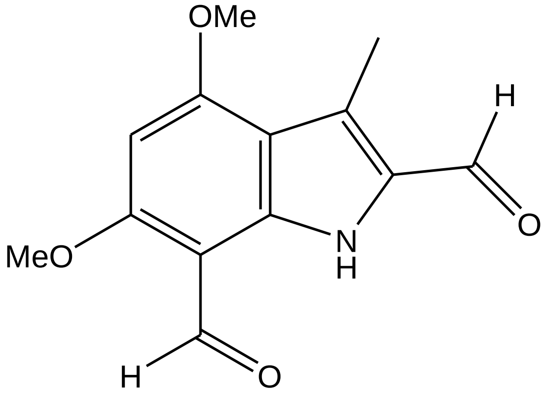
Compound	Found				Calc				Conductivity
	C	H	N	Cl	C	H	N	Cl	$\Omega^{-1}cm^2 mol^{-1}$
$[NiL^8][BF_4]$	49.1	4.3	14.9		49.1	4.2	14.8		121
$[NiL^9][BF_4]$	52.8	4.3	17.0		52.9	4.3	17.3		126
$[NiL^{10}][BF_4]$	51.1	3.8	18.1		51.2	3.7	18.0		127
$[NiL^{11}][BF_4]$	50.8	4.0	14.2		50.9	4.1	14.3		123
$[NiL^{12}][BF_4]$	54.6	4.1	16.5		54.8	4.1	16.6		124
$[NiL^{13}][BF_4]$	53.3	3.6	17.3		53.2	3.6	17.4		127
$[CuL^8][BF_4]$	48.9	4.2	14.6		48.8	4.2	14.8		125
$[CuL^9][BF_4]$	52.5	4.2	17.0		52.4	4.2	17.1		125
$[CuL^{10}][BF_4]$	50.6	3.7	17.8		50.7	3.7	18.0		123
$[CuL^{11}][BF_4]$	50.5	4.0	14.2		50.6	4.1	14.2		125
$[CuL^{12}][BF_4]$	54.2	4.0	16.4		54.3	4.0	16.4		128
$[CuL^{13}][BF_4]$	52.7	3.6	17.2		52.8	3.6	17.2		126
$[CoL^8(H_2O)][PF_6]$	44.2	4.1	13.4		44.0	4.1	13.3		123
$[CoL^9][PF_6]$	48.0	3.9	15.6		47.9	3.9	15.7		124
$[CoL^{10}][PF_6]$	46.2	3.3	16.3		46.2	3.4	16.4		124
$[CoL^{11}(H_2O)][PF_6]$	48.9	4.2	14.6		48.8	4.2	14.8		123
$[CoL^{12}][PF_6]$	49.8	3.7	15.0		49.9	3.7	15.1		122
$[CoL^{13}][PF_6]$	48.3	3.3	15.6		48.2	3.2	15.8		124
$[ZnL^8Cl]$	52.8	4.6	15.7		52.7	4.5	15.9		
$[ZnL^{11}Cl]$	54.5	4.4	15.2		54.4	4.3	15.3		
$[MnL^8Cl]$	53.7	4.7	16.2		53.6	4.6	16.2		
$[MnL^9Cl]$	58.4	4.7	19.0	6.9	58.5	4.7	19.1	6.9	
$[MnL^{10}Cl]$	57.0	4.2	20.1	7.3	57.0	4.1	20.2	7.3	
$[MnL^{11}Cl]$	55.2	4.5	15.4		55.4	4.4	15.6		
$[MnL^{12}Cl]$	60.4	4.5	18.2	6.6	60.4	4.5	18.3	6.6	
$[MnL^{13}Cl]$	59.0	4.0	19.2	6.9	59.0	4.0	19.3	7.0	
$[FeL^9Cl]$	58.5	4.7	18.9	6.9	58.5	4.7	19.1	6.9	
$[FeL^{10}Cl]$	56.9	4.2	20.1	7.3	56.9	4.2	20.2	7.3	
$[FeL^{12}Cl]$	60.2	4.4	18.1	6.6	60.3	4.5	18.2	6.6	
$[FeL^{13}Cl]$	58.8	3.9	19.2	6.9	58.9	4.0	19.2	7.0	

Table 2. Summary of ^{1}H NMR data of Zn(II) macrocyclic complexes.

Compound	^{1}H NMR in DMSO-d_6
[Zn**L**^{8}Cl]	1.06 (3H, s, CH_3); 1.69 (2H, m, CH_2); 1.90 (3H, dt, 2CH); 2.73 (4H, m, CH); 3.20 (6H, s, $2OCH_3$); 3.35 (4H, t, $2CH_2$); 3.79 (4H, t, $2CH_2$); 7.63 (2H, s, 2HC=N); 7.10-7.62 (6H, m, ArH).
[Zn**L**^{11}Cl]	1.04 (3H, s, CH_3); 1.68 (2H, m, CH_2); 1.92 (3H, dt, 2CH); 2.75 (4H, m, CH); 3.18(6H, s, $2OCH_3$); 3.36 (4H, t, $2CH_2$); 3.75 (4H, t, $2CH_2$); 7.87 (2H, s, 2HC=N); 7.10-7.62 (6H, m, ArH).

3. Results and discussion

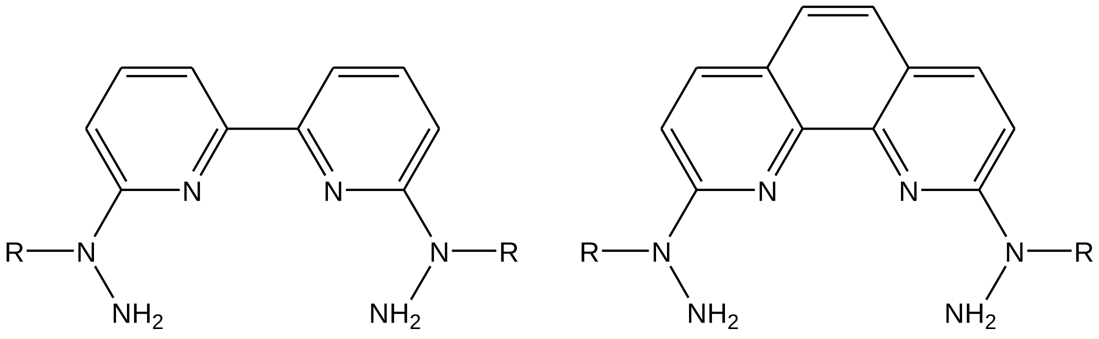
There have been very few reports of macrocyclic ligands which incorporate indole moieties within the cyclic framework. The condensation of dicarbonyls with diamines or bis(hydrazines) provides a facile route to ring closure, and indoledialdehydes or indolediketones are obvious candidates for such cyclisation reactions. Indoles differ from related pyridines in possessing an acidic NH functionality, which allows the preparation of macrocycles which may bind metals with concomitant deprotonation. Black and co-workers developed an effective synthetic route to 2,7-diformyl-3-methyl-4,6-dimethoxyindole (**HL**) (Chart 1) and demonstrated that macrocyclic complexes may be obtained from template condensations with α,ω-diamines [45,46]. Black also demonstrated the facile preparation of other macrocyclic ligands containing three indolyl subunits [47] and 2,2'-biindolyl moieties [48]. The similarity in behaviour between (**HL**) and 2,6-diformylpyridine led us to investigate the reactions of **HL** with 6,6'-bis(hydrazino)-2,2'-bipyridines and 2,9-bis(hydrazino)-1,10-phenanthrolines in an attempt to prepare hydrazone-based macrocycles incorporating an indolyl functionality.



HL

Chart 1. 2,7-Diformyl-3-methyl-4,6-dimethoxyindole.

The dialdehyde **HL** was prepared by the literature method in 44% overall yield from 3,5-dimethoxyaniline and ethyl oxomalonate [45]. The reactions of the bis(hydrazines) **L**^{2}-**L**^{7} (Chart 2) with the dialdehyde **HL** in the absence of metal-ions were briefly investigated. In all cases, reaction in MeOH in the presence or absence of acid resulted in the formation of intractable, dark-coloured polymeric materials and none of the desired macrocycles **HL**^{8}-**HL**^{13}. We did not further pursue this synthetic method, and concentrated instead upon metal-directed template assembly of the macrocyclic systems.

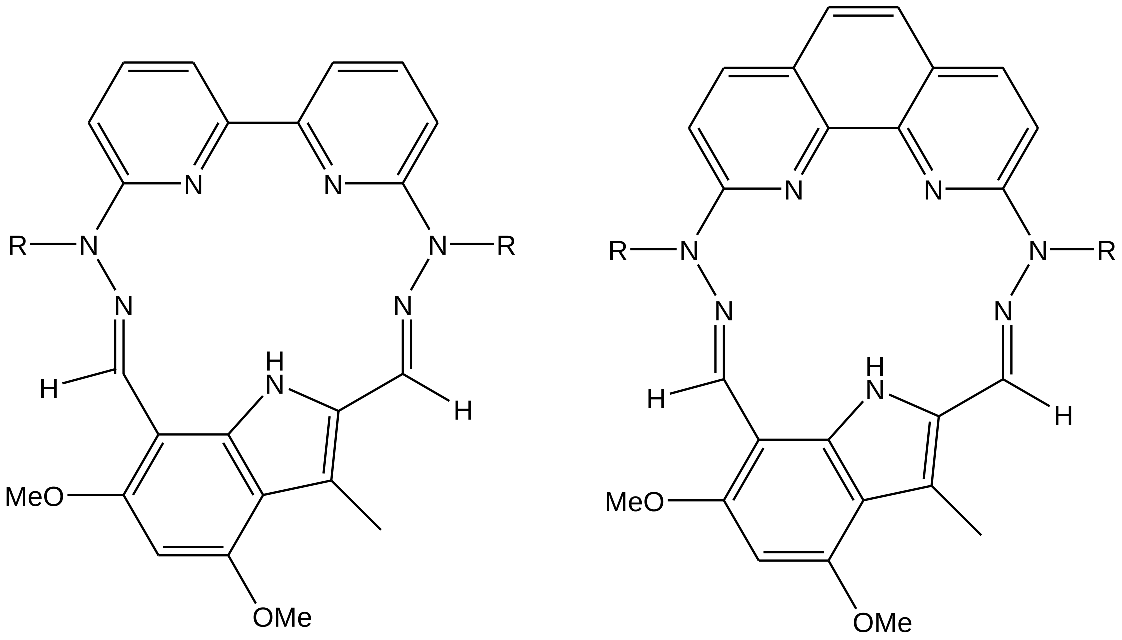


L^2 R = CH_2CH_2OH
L^3 R = CH_3
L^4 R = H

L^5 R = CH_2CH_2OH
L^6 R = CH_3
L^7 R = H

Chart 2. 2,2’-Bipyridine and 1,10-phenanthroline bis-hydrazines.

We concentrated upon template reactions involving **HL** and $\mathbf{L}^{2\text{-}7}$. The reaction of the hyrazines with **HL** in refluxing MeOH in the presence of manganese(II) acetate, cobalt(II) acetate, copper(II) acetate or zinc(II) acetate resulted in the formation of coloured solutions from which coloured solids were precipitated upon the addition of ammonium hexafluorophosphate or sodium tetrafluoroborate. In some cases, triethylamine was added to the reaction mixture and it was observed that the colour changes occurred more rapidly in the presence of the base. This is consistent with the formation of metal complexes of the deprotonated macrocyclic ligands $\mathbf{HL}^{8\text{-}13}$ (Chart 3).



L^8 R = CH_2CH_2OH
L^9 R = CH_3
L^{10} R = H

L^{11} R = CH_2CH_2OH
L^{12} R = CH_3
L^{13} R = H

Chart 3. Macrocyclic ligands incorporating indoledialdehyde.

In the case of the nickel(II) templated reactions, the final reaction solutions were orange-yellow in colour. Concentration of these solutions followed by the addition of methanolic $Na[BF_4]$ solution resulted in the precipitation of orange-brown solids in 50-70% yield. Recrystallisation from MeOH or DMF-MeOH gave orange microcrystalline products which analysed for $[Ni\mathbf{L}^{8\text{-}13}][BF_4]$ after prolonged drying *in vacuo*. These complexes are soluble in nitromethane to give orange solutions which behave as 1:1 electrolytes. The infra-red spectra of the complexes exhibit no amine absorptions and no carbonyl absorptions in the range 1600-2000 cm^{-1}, but do show strong absorptions at 1590-1580 cm^{-1} assigned to imine stretching modes. The strong NH stretching mode observed in the free ligand **HL** is absent from these complexes. All of these data are fully in accord with the formation of nickel(II) complexes of the deprotonated macrocyclic ligands.

Repetition of the above reactions with copper(II) acetate or cobalt(II) acetate resulted in the formation of the complexes $[Cu\mathbf{L}^{\mathbf{8-13}}][BF_4]$ or $(Co\mathbf{L}^{\mathbf{8-\ 13}}(H_2O)_n][PF_6]$ (n = 0,1). The copper(II) complexes were obtained as dark-brown microcrystalline solids whereas the cobalt(II) species were orange-brown. In each case, the I.R. spectra showed no carbonyl or NH absorptions, but strong imine stretches in the range 1590-1595 cm^{-1}. Those of the cobalt(II) complexes which analysed as containing a water molecule also showed absorptions in the 1630-1640 cm^{-1} region assigned to coordinated water. The cobalt(II) complexes are all electrochemically active, and in acetonitrile solution exhibit a reversible or quasi-reversible oxidation (Co^{II}/Co^{III}) at +0.1-+0.2 V vs. Ag/AgCl. The magnetic moments of the cobalt(II) complexes are in the range 4.50-4.70 B.M., in accord with the spin-only formula. These complexes all behave as 1:1 electrolytes in nitromethane solution.

Slightly different behaviour is observed in the template condensation of **HL** with $\mathbf{L}^{\mathbf{2-7}}$ with zinc(II) or manganese(II) acetate in MeOH solution. In these cases, orange or yellow solids were precipitated from the reaction mixture, but these did not behave as pure macrocyclic products and were contaminated with metal hydroxides. In order to avoid the precipitation of metal hydroxides, the solutions were buffered by substitution of the salts $[\mathbf{HL}^{\mathbf{2-7}}]Cl$ in the presence of triethylamine. This resulted in the formation of clean products, for which microanalysis indicated the formulations $[Zn\mathbf{L}^{\mathbf{8,11}}Cl]$ and $[Mn\mathbf{L}^{\mathbf{8-13}}Cl]$ respectively. These molecular species exhibited parent ions in their mass spectra all showing the correct isotopomer distributions. All of these complexes behave as non-electrolytes in DMSO solution. Once again, the I.R. spectra showed no carbonyl or NH absorptions, but strong imine stretches in the range 1590-1595 cm^{-1}. Similar complexes, $[Fe\mathbf{L}^{\mathbf{9,10,12,13}}CI]$, are obtained by the use of iron(II) chloride as a template. The manganese(II) and iron(II) complexes are high-spin and each possesses magnetic moments of 5.8-6.0 B.M.

The ^{1}H NMR spectra of the Zn(II) complexes $[Zn\mathbf{L}^{\mathbf{8}}Cl]$ and $[Zn\mathbf{L}^{\mathbf{11}}Cl]$ have been investigated in strong polar solvents such as DMSO–d_6. The spectra are concentration independent and exhibited the number of peaks expected for each molecular structure, which suggests that the discrete anionic macrocycle complexes remain intact in solution.

Repeated attempts to obtain X-ray quality crystals of any of these complexes were unsuccessful. In every case, very small microcrystals or powders were obtained. In the absence of crystallographic data, we can only propose tentative structures for these complexes. The I.R. data strongly supports the formation of complexes of the desired macrocyclic ligands rather than of the acyclic precursors or acyclic reaction products. The absence of carbonyl absorptions is particularly indicative, as is the appearance of bands assigned to imine C=N stretches. In all cases, the metal complexes contain the deprotonated ligands. Once again, the I.R. data supports this and shows the loss of the pyrrolic NH absorption. The overall stoichiometry of the complexes also supports this, with the formation of mono-cationic $(M\mathbf{L}^{\mathbf{8-13}})$ species.

The neutral zinc(II), iron(II) and manganese(II) complexes contain coordinated chloride, and the most likely structure is a six-coordinate one containing a pentagonal-based pyramidal metal center, with the macrocyclic ligand occupying the basal plane and the chloride the axial site (Figure 1). This is strikingly reminiscent of the pentagonal-based pyramidal structures we have previously described for chloro- complexes of the pentadentate macrocyclic ligands obtained from the template condensation of $\mathbf{L}^{\mathbf{2}}$-$\mathbf{L}^{\mathbf{7}}$ with 2,6-pyridinedicarbonyls in the presence of metal chlorides [4-29].

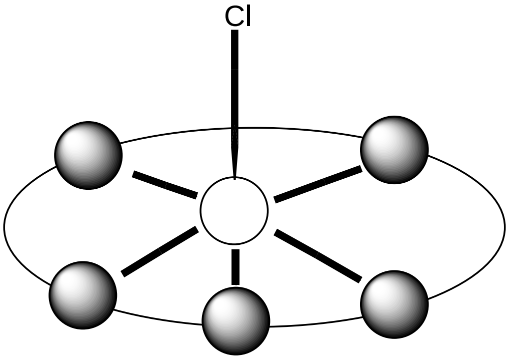


Figure 1. Proposed structure of the six-coordinate zinc(II), iron(II) and manganese(II) complexes, $[M\mathbf{L}^{\mathbf{8-13}}]Cl$.

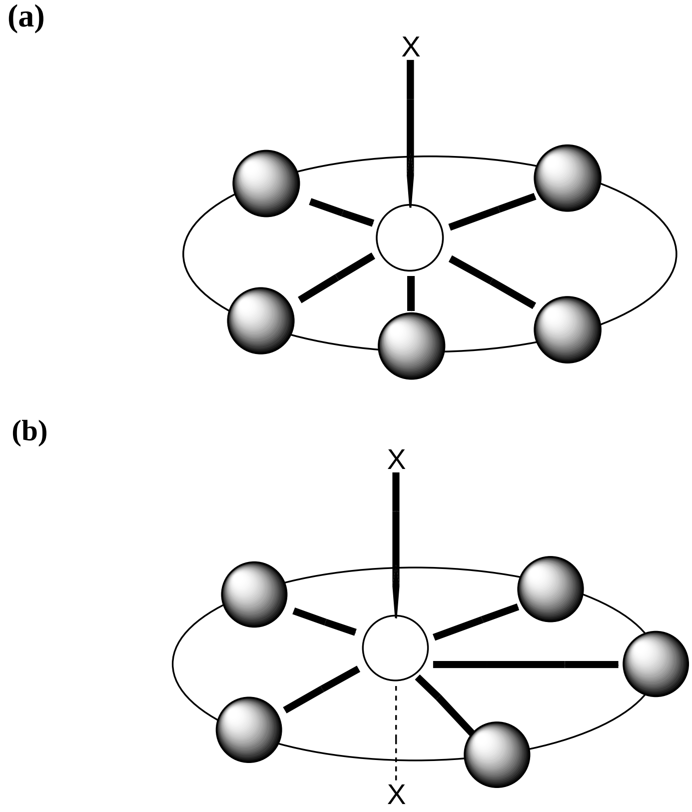


Figure 2. (a) Proposed structure of the six-coordinate nickel(II), cobalt(II) and copper(II) complexes, [**ML$^{9/10}$**][BF$_4$]; (b) Proposed structure of the seven-coordinate nickel(II), cobalt(II) and copper(II) complexes, [**ML$^{9/10}$**][BF$_4$].

The structures of the nickel(II), cobalt(II) and copper(II) complexes is less certain. Drying the complexes to obtain analytically pure samples results in solvent loss and the formation of complexes analyzing as [**ML$^{9/10}$**][BF$_4$]. In the light of our structural studies with related ligands [4-29] we suggest that these complexes are six- (Figure 2a) or seven-coordinate (Figure 2b) species, but in the absence of further structural data, we cannot make unambiguous assignments of their structures. In the case of some of the cobalt(II) complexes, we have evidence for the presence of one strongly associated water molecule, and cannot eliminate a structure such as shown in Figure 3, in which the condensation has resulted in the formation of one imine and aminol functionality.

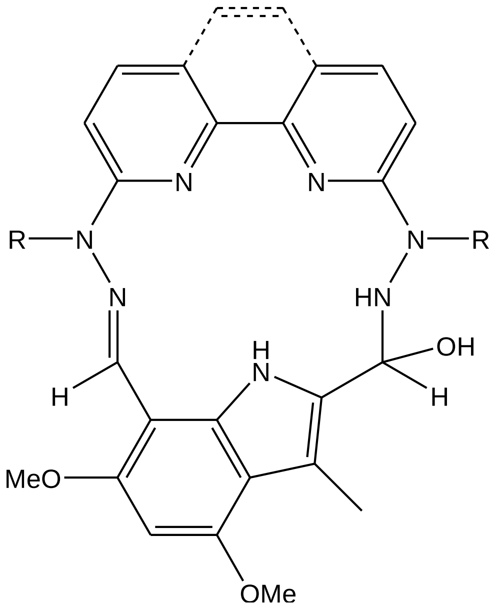


Figure 3. Proposed structures of some cobalt(II) complexes containing one imine and an aminol functionality.

4. Conclusion

The indoledialdehyde (**HL**) is a versatile dicarbonyl for incorporation into macrocyclic ligands which may be deprotonated to yield anionic species. Although clean macrocyclic complexes may be obtained from template condensations, we have been unable to grow X-ray quality crystals to unambiguously confirm the structures.

5. Acknowledgement

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