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Derivatized Pentadentate Macrocyclic Ligands and Their Transition Metal Complexes

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مشتقات المركبات الخماسية الحلقة ومعقداتها مع العناصر الإنتقالية

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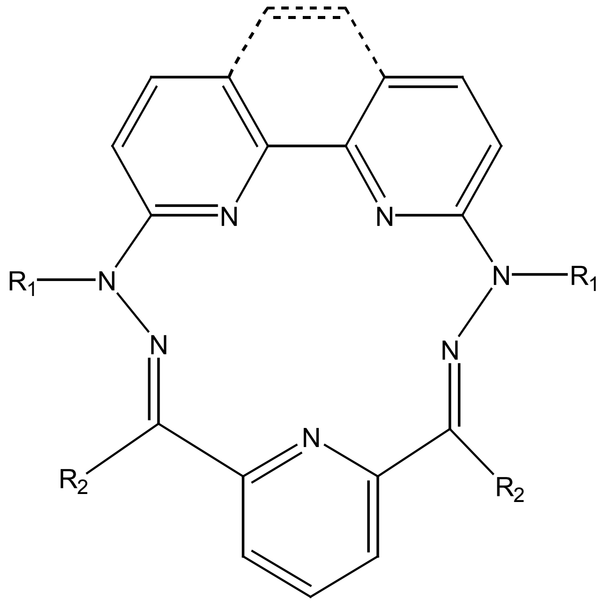
خلاصة: تفاعلات مجموعة الهيدروكسي اثيل في المركبات خماسية الحلقة: 1,11- ثنائي (-'2,هيدروكسي اثيل)-21,17;16,12;8,4- ثلاثي نايترايلو -11,10,2,1- رباعي ازا سيكلوهينيكوسا-20,18,14,12,9,6,4,2- أكتايين (ل^2) المشتق من تفاعلات التكاثف من 6,2– ثنائي بريدين الدهايد مع 6',6- ثنائي('2- هيدروكسي اثيل هايدرازينو) -2',2- ثنائي البيردين (ل^1) بتفاعلات الاسترة كانت إيجابية وتفاعل مجموعة الهيدروكسيل اثيل في هذه الحلقات مع مركبات الثيونيل الكلورايد انتج مشتق الكلورواثيل. المعقدات الفلزية من هذه المركبات ل$^{3-6}$ ذات الصيغة العامة $ML^{3-6}.X_2.nH_2O$ (M = فلزات الدورة الأولى من العناصر الإنتقالية) درست وحضرت أيضاً.

ABSTRACT:The reaction of the pendant hydroxyethyl group in the planar pentadentate macrocyclic ligand,1,11-bis(2’-hydroxyethyl)-4,8;12,16;17,21-trinitrilo-1,2,10,11-tetraazacyclohenicosa- 2,4,6,9,12,14,18,20-octaene (L^2), derived from the condensation of 2,6-pyridinedialdehyde with 6,6’-bis(2’-hydroxyethylhydrazino)-2,2’-bipyridine (L^1), has been investigated. Esterification reactions are facile, and the reaction of the hydroxyethyl-substituted macrocycle with thionyl chloride yields a chloroethyl derivative. Metal complexes of the new derivatized macrocyclic ligands L^{3-6} having general formula $ML^{3-6}X_2.nH_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn) are readily prepared.

KEYWORDS: Macrocyclic Ligands, Coordination Complexes, Transition Metals, Esterification, Functional Group Interconversion.

1. Introduction

Macrocyclic compounds of biological significance, such as the porphyrin, chlorophyll and corrin complexes have been studied for many years (Smith, 1975). More recently, other macrocyclic ligands and their metal complexes have been synthesized (Constable, 1999). The wide range of interest in the synthetic macrocyclic ligand complexes has arisen partly because their similarity to certain biological macrocyclic systems has enabled them to be used as models in the study of these systems. Interest in the synthetic macrocyclic systems also arises due to the unusual properties they may exhibit in their own right. The tendency for a macrocyclic complex to be more stable with respect to ligand dissociation than a comparable open-chain multidentate ligand complex, over and above the chelate affect, is well documented. This phenomenon, termed the ‘Macrocyclic Effect’ (Cabbinnes and Margerum, 1969) is thought to have both kinetic and thermodynamic origins. Another interesting aspect is the unusual stereochemical arrangement that may be formed on coordination of the macrocyclic ligands to the metal centers. This is particularly true of the pentadentate N_5-donor macrocyclic ligands involving π-electron delocalization around the ring. A rigid stereochemical arrangment is often imposed on the metal that would not occur in the absence of the macrocyclic ligand. The geometry of unsaturated macrocycles is generally planar due to the more favorable overlap of π-symmetry orbitals. Planar pentadentate N_5-donor macrocyclic ligands may form five coordinate planar, six-coordinate pentagonal-based pyramidal and seven-coordinate pentagonal bipyramidal complexes with metal ions (Melson, 1979; Lindoy, 1989). We have been interested in the design, synthesis and coordination chemistry of a series of pentadentate N_5-donor macrocycles involving poly-pyridine groups (Figure 1).



R_1 = H, CH_3 ; R_2 = H, CH_3

Figure 1. Polypyridyl N_5-macrocycles.

The rationale for choosing pyridine derivatives as components within the macrocycle framework is that they readily reduce to radical ions, thereby imparting interesting redox properties to the macrocyclic complexes. The fused rings of 2,2'-bipyridine/1,10-phenanthroline are also expected to impart additional rigidity to the macrcocyle rings. Pentadentate macrocyclic ligands of this type are readily prepared by template or transient template condensations of hydrazino-substituted 2,2'-bipyridines (Ansell *et al* 1982a, 1982b, 1983), 1,10-phenanthroline or 2,2':6',2"-terpyridines with 2,6-pyridine dicarbonyl (Constable *et al*, 1985). We have synthesized pentadentate macrocycle L^2 with pendant hydroxyethyl group that allows further structural development of the macrocycle by derivatization and the design of biometic systems (Ansell *et al*, 1983). In this paper we wish to describe the synthesis and coordination chemistry of some such derivatized macrocyclic ligands L^{3-6} (Figure 2).

2. Materials and Method

All reagents were purchased from Sigma Aldrich and used without further purification. Solvents were dried and distilled before use by standard methods. All reactions were performed under N_2. Infrared spectra were recorded in compressed KBr pellet on Perkin Elmer 983 spectrophtometer. ^{1}H NMR spectra were recorded on Bruker WM 250 or AM 400 spectrometers. Fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on a Kratos MS 50 mass spectrometer. Microanalysis was performed in the Department of Chemistry, University of Cambridge, U.K. Conductance measurements were made using a Wayne Kerr

Universal Bridge. The macrocyclic ligand salt $[H_2L^2][PF_6]_2$ was prepared as previously described (Chung *et al* 1990).

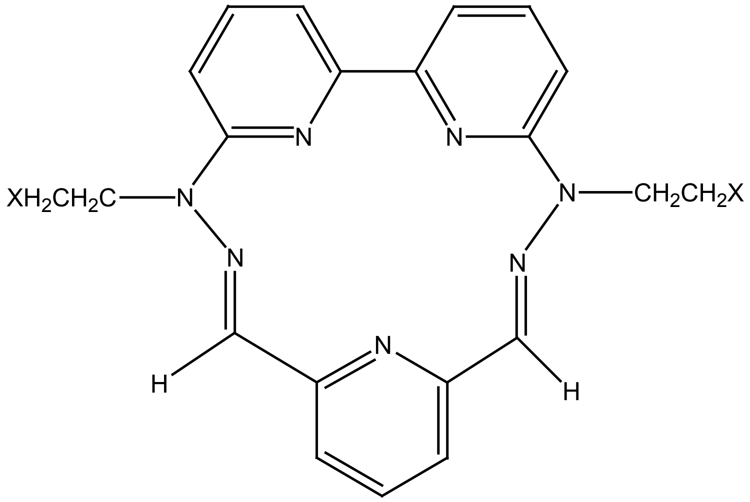


Figure 2. Derivatized N_5-macrocylic ligands.
L^2: X = OH; L^3: X = O_2CCH_3 ; L^4: X = $O_2CCH_2CH_3$;
L^5: X = $O_2CC_6H_5$; L_6: X = Cl

3. Synthesis of Derivatized Macrocyclic Ligands L^{3-6}

3.1 Synthesis of $[H_2L^3][PF_6]_2$

A solution of $[H_2L^2][PF_6]_2 \cdot H_2O$ (0.064 g, 0.09 mmol) in dry acetonirile (50 mL) was stirred for 12 hours with acetyl chloride (5 mL). After twelve hours the orange solution was concentrated in *vacuo* to 5 mL volume and treated with water (50 mL) and sufficient acetonitrile to redissolve the initial precepitate. The solution was then filtered and the filtrate treated with saturated aqueous $[NH_4][PF_6]$ solution (10 mL). The orange solution was then slowly concentrated in *vacuo* to yield orange-red crystals of $[H_2L^3][PF_6]_2 \cdot H_2O$ (0.07 g, 96%). Anal. Found: C, 36.6; H, 3.4; N, 12.4. Calc. for $C_{25}F_{12}H_{31}N_7O_6P_2$: C, 36.8; H, 3.6; N, 12.0%. Infrared, 1741 cm^{-1}. EI-MS (*m/z*): 487.

3.2 Synthesis of $[H_2L^4][PF_6]_2$

The procedure was analogous to that described above for $[H_2L^3][PF_6]_2$. Yield: 75% as orange-red crystals of $[H_2L^4][PF_6]_2 \cdot H_2O$. Anal. Found: 39.5; H, 3.6; N, 11.9. Calc. for $C_{27}F_{12}H_{33}N_7O_5P_2$: C, 39.3; H, 3.5; N, 11.9%. Infrared, 1737 cm^{-1}. EI-MS (*m/z*): 515.

3.3 Synthesis of $[H_2L^5][PF_6]_2$

A solution of $[H_2L^2][PF_6]_2 \cdot H_2O$ (0.10 g, 0.14 mmol) in dry acetonirile (50 mL) was heated to reflux for 36 hours with benzoyl chloride (0.7 mL). The resulting orange solution was concentrated in *vacuo* to 5 mL volume when an oil formed. Water (25 mL) was added and the mixture heated to 90ºC for 10 minutes to hydrolyse excess benzoyl chloride. The solution was then extracted with diethyl ether (2 x 20 mL) and the resulting aqueous suspension treated with sufficient acetonitrile to give a clear solution. This was then filtered and the filtrate treated with saturated aqueous $[NH_4][PF_6]$ solution (10 mL). The orange solution was then slowly concentrated in *vacuo* to yield orange-red crystals of $[H_2L^5][PF_6]_2 \cdot H_2O$ (0.05 g, 40%). Anal. Found: C, 68.46 ; H, 5.18 ; N, 15.89. Calc. for $C_{35}F_{12}H_{31}N_7O_5P_2$: C, 68.6; H, 5.1; N, 16.0%. Infrared, 1720 cm^{-1}.

Table 1: Analytical data for transition metal complexes of L^{3-6} .

Compound	Found %			Calc. %		
	C	H	N	C	H	N
$[MnL^3(H_2O)_2][PF_6]_2\cdot H_2O$	34.04	3.56	11.21	33.89	3.53	11.07
$[FeL^3(H_2O)_2][PF_6]_2\cdot H_2O$	34.12	3.63	10.98	33.86	3.52	11.06
$[CoL^3][PF_6]_2\cdot H_2O$	34.99	3.64	11.39	35.16	3.66	11.48
$[NiL^3(H_2O)_2][PF_6]_2\cdot MeCN$	35.58	3.46	12.21	35.53	3.42	12.28
$[CuL^3(H_2O)_2][PF_6]_2\cdot H_2O$	33.65	3.52	11.4	33.57	3.49	10.96
$[ZnL^3(H_2O)_2][PF_6]_2\cdot H_2O$	33.28	3.42	10.89	33.50	3.49	10.94
$[MnL^4(H_2O)_2][PF_6]_2\cdot H_2O$	35.41	3.53	10.69	35.48	3.61	10.73
$[FeL^4(H_2O)_2][PF_6]_2\cdot H_2O$	35.38	3.68	10.63	35.45	3.61	10.72
$[CoL^4][PF_6]_2\cdot H_2O$	36.71	3.72	11.09	36.77	3.75	11.12
$[NiL^4(H_2O)_2][PF_6]_2\cdot MeCN$	36.98	3.48	11.82	37.02	3.51	11.91
$[CuL^4(H_2O)_2][PF_6]_2\cdot H_2O$	35.28	3.47	10.72	35.15	3.58	10.63
$[ZnL^4(H_2O)_2][PF_6]_2\cdot H_2O$	36.27	3.65	10.89	36.18	3.71	10.94
$[MnL^5(H_2O)_2][PF_6]_2\cdot H_2O$	29.97	2.57	11.67	30.10	2.53	11.70
$[FeL^5(H_2O)_2][PF_6]_2\cdot H_2O$	29.98	2.58	11.74	30.07	2.52	11.69
$[CoL^5][PF_6]_2\cdot H_2O$	31.25	2.72	12.18	31.30	2.63	12.17
$[NiL^5(H_2O)_2][PF_6]_2\cdot MeCN$	32.07	2.47	13.01	31.94	2.45	12.96
$[CuL^5(H_2O)_2][PF_6]_2\cdot H_2O$	29.85	2.44	11.63	29.79	2.50	11.59
$[ZnL^5(H_2O)_2][PF_6]_2\cdot H_2O$	28.09	2.28	11.01	28.14	2.36	10.94
$[MnL^6(H_2O)_2][PF_6]_2\cdot H_2O$	50.23	3.69	11.63	50.17	3.73	11.70
$[FeL^6(H_2O)_2][PF_6]_2\cdot H_2O$	50.19	3.68	11.79	50.11	3.73	11.69
$[CoL^6][PF_6]_2\cdot H_2O$	52.23	3.94	12.24	52.16	3.88	12.17
$[NiL^6(H_2O)_2][PF_6]_2\cdot MeCN$	48.56	3.59	13.05	48.61	3.61	12.96
$[CuL^6(H_2O)_2][PF_6]_2\cdot H_2O$	49.72	3.71	11.67	49.66	3.69	11.59
$[ZnL^6(H_2O)_2][PF_6]_2\cdot H_2O$	46.94	3.52	11.01	46.89	3.49	10.94

3.4 Synthesis of $[H_2L^6][PF_6]_2$

A solution of $[H_2L^2][PF_6]_2\cdot H_2O$ (0.05 g, 0.07 mmol) in dry acetonirile (25 mL) was heated to reflux for 3 hours with thionyl chloride (1 mL). After this period the orange solution was evaporated to dryness in *vacuo* and the residue dissolved in acetonitrile (0.5 mL). Diffusion of diethyl ether vapour into this solution yielded orange-red needles of $[H_2L^6][PF_6]_2$ (0.03 g, 67%). Anal. Found: 34.34; H, 2.97; N, 13.62. Calc. for $C_{21}Cl_2F_{12}H_{21}N_7P_2$: C, 34.42; H, 2.93; N, 13.68%. FAB-MS (*m/z*): 439, 441, 443.

4. Synthesis of Metal Complexes of Derivatized Macrocyclic Ligands

4.1 Metal Complexes of L^3

A solution of $[H_2L^3][PF_6]_2 \cdot 2H_2O$ in 3:1 acetonitrile/methanol was treated with a solution of 1 equivalent of an appropriate metal(II) acetate dissolved in the minimum volume of methanol. The mixture was then heated to reflux for 15 minutes, concentrated to 1/5th volume in *vacuo* and treated with saturated $[NH_4][PF_6]$ solution. The products were collected by filtration and dried to yield the desired complexes in a good yield (typically > 75%). Analytical data are presented in Table 1.

4.2 Metal Complexes of L^4

The procedure was analogous to that used for metal complexes of L^3. The desired products were isolated in > 80% yield. Analytical data are presented in Table 1.

4.3 Metal Complexes of L^5

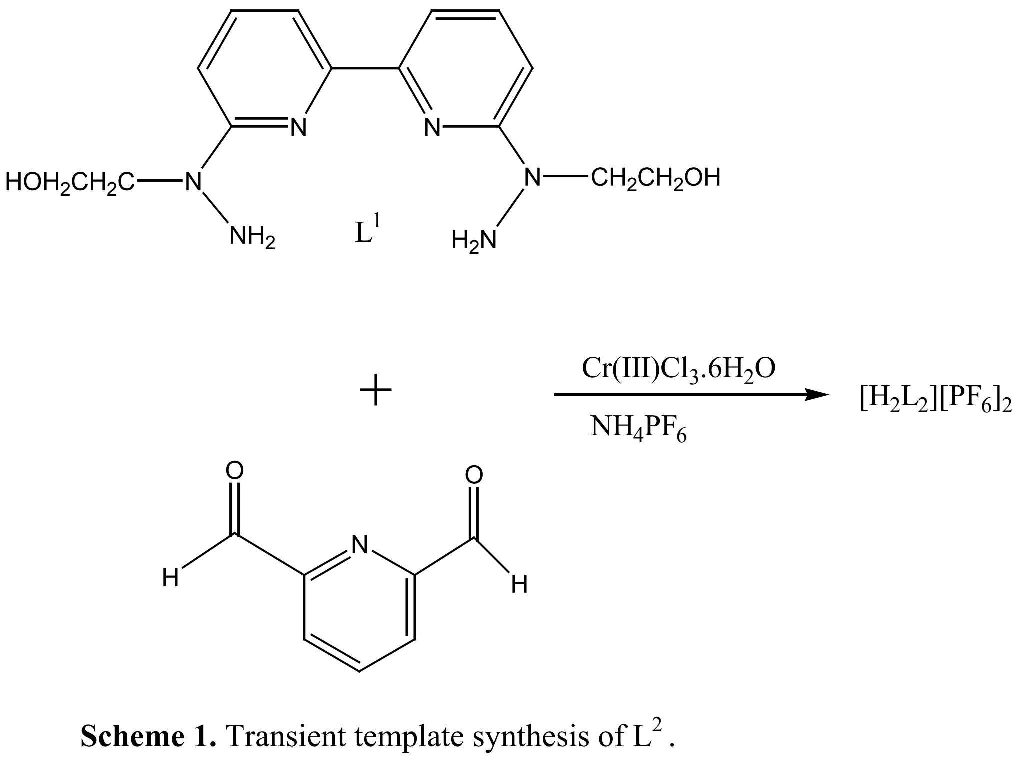
The procedure was analogous to that used for metal complexes of L^3. The products were isolated in > 80% yield. Analytical data are presented in Table 1.

4.4 Metal complexes of L^6

The procedure was analogous to that used for metal complexes of L^3. The products were isolated in respectable yields (typically > 65%). Analytical data are presented in Table 1.

5. Results and Discussion

Planar pentadentate macrocyclic ligands such as L^2 may be prepared by transient template condensations of the appropriate hydrazines L^1 with 2,6-pyridinedialdehyde or 2,6 diacetylpyridine. These ligands, which are of particular interest in bearing a functionalized substituent that may be further derivatized to yield encapsulating or capped macrocycles. The open-chain bishydrazines are readily prepared by the reaction of a suitable dihalo compound with α-hydroxyethylhydrazine. The free macrocyclic ligand L^2 is best prepared as the hydrochloride or other salt by transient template condensations of 6,6'-bis(2'-hydroxyethylhydrazino)-2,2'-bipyridine (L^1) with 2,6- pyridinedialdehyde in the presence of chromium(III) chloride (Scheme 1).



Scheme 1. Transient template synthesis of L^2.

As an initial investigation into the further functionalization of these macrocyclic ligands we studied acylation reactions of L^2. Solutions of $[H_2L^2][PF_6]_2$ in acetonitrile changed in color from red to orange upon stirring overnight with excess of acetyl chloride. Treatment of this orange solution with water followed by $[NH_4][PF_6]$ resulted in the formation of an orange crystalline product. In the presence of an excess of acetyl chloride we anticipated the formation of the bisacetylated ligand L^3, and microanalysis was in accord with the orange product being formulated $[H_2L^3][PF_6]_2 \cdot 2H_2O$. The conversion proceeds in a near-quantitative manner, and isolated yields of 96% of the salt were obtained. The EI mass spectrum of the salt exhibits a parent ion for $\{L^3\}^+$ at *m/z* 487. The infrared spectrum of the compound showed a single strong carbonyl absorption at 1741 cm^{-1} as expected for the bisacetylated compound. The isolated hexafluorophosphate salt was insufficiently soluble in D_2O or CD_3OD to obtain ^1H NMR spectra in these solvents, but broadened spectra could be obtained in CD_3CN or CD_3COCD_3. Unfortunately, the resonances assigned to the acetyl groups were obscured in these solvents, and it was necessary to use CD_3SOCD_3 solution, and this effect was again observed with $[H_2L^3][PF_6]_2$. The acetyl protons appeared as a singlet (δ 1.91) and integration confirmed that a bisacetylated derivative had been obtained.

A similar smooth reaction occurred when an acetonitrile solution of $[H_2L^2][PF_6]_2$ was stirred with propionyl chloride, and after the usual work up, $[H_2L^4][PF_6]_2$ was obtained as an orange crystalline solid in 75% yield. Once again, microanalysis was consistent with this formulation, and the EI mass spectrum exhibited a parent ion at *m/z* 515. The infrared spectrum showed a singlet strong carbonyl absorption at 1737 cm^{-1} as expected for the desired bisacylated product. This product is considerably more soluble in CD_3OD than $[H_2L^4][PF_6]_2$, and sharp well-resolved ^1H NMR spectra could be obtained in this solvent. The most evident feature of the spectrum are the triplet (δ 1.01, 6H, J 7.5 Hz) and quartet (δ 2.26, 4H, J 7.5 Hz) assigned to the propionyl group. Similar acylations have been demonstrated for other alkanecarboxylic acids, and the reaction appeared to be general.

We also considered the formation of esters with arenecarboxylic acids, and investigated the reaction of $[H_2L^2][PF_6]_2$ with benzoyl chloride under a variety of experimental conditions. The macrocycle was recovered unchanged after stirring a solution of $[H_2L^2][PF_6]_2$ in acetonitrile with benzoyl chloride overnight. We could not obtain benzoylated products from attempted acylation under Schotten-Baumann conditions. Eventually, the desired bisbenzoylated compound was obtained after heating an acetonitrile solution of $[H_2L^2][PF_6]_2$ with an excess of benzoyl chloride to reflux for 36 hours. The product of this reaction tended to be oily, but eventually orange-red crystals of $[H_2L^5][PF_6]_2$ were obtained by repeated crystallization from aqueous acetonitrile. The mass spectrum did not exhibit a molecular ion, but merely showed a fragmentation peak assigned to $\{L^2\}^+$. The infrared spectrum provides firm evidence for the formation of the desired derivatized macrocyclic product and shows strong carbonyl stretching absorption at 1720 cm^{-1}, typical of benzoate esters. The ^1H NMR spectrum of the compound in CD_3SOCD_3 solution is of interest in showing both broadened and sharp resonances in the aromatic region, Figure 3a. Integration of spectra obtained using very long relaxation delays between pulses indicated that the ratio of the sharp peaks to the broadened peaks was 10:11; this is in accord with the resonances assigned to protons in the macrocyclic ring being broadened as previously noted, but those of the phenyl groups being sharp. The ^1H NMR spectrum of the solution of $[H_2L^5][PF_6]_2$ shows temperature dependent behaviour, and upon heating to 370 K is significantly sharpened, Figure 3b.

In addition to esterification, we have also investigated other reactions of pendant hydroxyethyl substituent in L^2. Numerous attempts to prepare the tosylates by reaction with 4-toluenesulphonyl chloride in a wide range of experimental conditions were unsuccessful. Generally, the products were intractable tars. We have had rather more success in the reaction with thionyl chloride to yield L^6. Upon heating acetonirile solutions of $[H_2L^2][PF_6]_2$ with thionyl chloride, orange solutions were obtained, from which the salt $[H_2L^6][PF_6]_2$ could be isolated as orange needles. The microanalysis is in accord with this formulation, and the FAB mass spectrum exhibited a parent ion at *m/z* 439, 441, 443 showing the expected isotopomeric distribution for a compound containing two chlorine atoms. No absorptoions due to hydroxy groups are observed in the infrared spectrum of the compound. Once again, the complex exhibits a broadened ^{1}H NMR spectra in CD_3SOCD_3 solution.

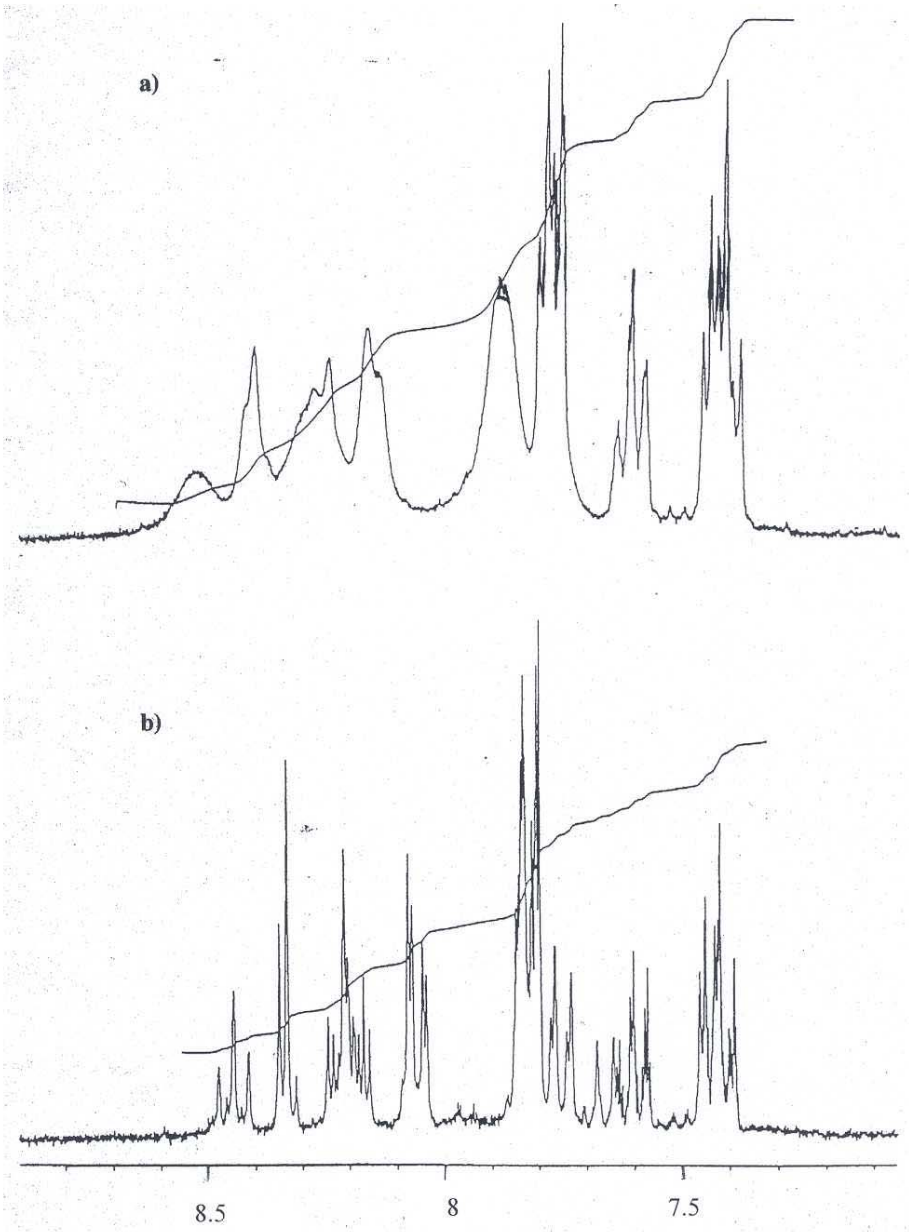


Figure 3. ^{1}H NMR spectrum of a CD_3SOCD_3 solution of $[H_2L^5][PF_6]_2$ at: a) 298 K and b) 370 K.

We have made preliminary studies of the coordination behaviour of the derivatized ligands. The salts $[H_2L^{3-6}][PF_6]_2$ react smoothly with metal acetates in boiling methanolic solution to yield metal complexes, which may be recrystallized from aqueous acetonitrile to yield the crystalline complexes $[ML^{3-6}][PF_6]_2 \cdot nH_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn). In the absence of any structural data we propose that these complexes possess pentagonal bipyramidal geometries, in which the two axial sites are occupied by coordinated water. The infrared spectra exhibited sharp absorptions at 3604 cm^{-1} due to the coordinated water molecules. In the solid state, considerable shifts of the carbonyl stretching frequency occurred upon coordination of L^{3-5}, Table 2. This suggests that there is significant hydrogen-bonding interaction between the coordinated water and the carbonyl groups. Conducivity in nitromethane (see Table 2) indicates that all the complexes are 2:1 electrolytes (Geary, 1971) corresponding to the presence of two counter ions per macrocyclic complex. Taken in conjunction with the analytical data and infrared spectra, conductivity measurements provide very strong evidence for pentagonal bipyramidal coordination geometry for transition metal complexes of the derivatized macrocyclic ligands.

Table 2: Carbonyl stretching frequency and conductivity of the complexes.

	ν_{CO} (cm^{-1})	Λ ($Ohm^{-1}cm^2 mole^{-1}$)
$[MnL^3(H_2O)_2][PF_6]_2{\cdot}H_2O$	1716	165
$[FeL^3(H_2O)_2][PF_6]_2{\cdot}H_2O$	1714	160
$[CoL^3][PF_6]_2{\cdot}H_2O$	1707	167
$[NiL^3(H_2O)_2][PF_6]_2{\cdot}MeCN$	1723	162
$[CuL^3(H_2O)_2][PF_6]_2{\cdot}H_2O$	1739	158
$[ZnL^3(H_2O)_2][PF_6]_2{\cdot}H_2O$	1723	164
$[MnL^4(H_2O)_2][PF_6]_2{\cdot}H_2O$	1715	164
$[FeL^4(H_2O)_2][PF_6]_2{\cdot}H_2O$	1716	163
$[CoL^4][PF_6]_2{\cdot}H_2O$	1710	166
$[NiL^4(H_2O)_2][PF_6]_2{\cdot}MeCN$	1721	165
$[CuL^4(H_2O)_2][PF_6]_2{\cdot}H_2O$	1737	160
$[ZnL^4(H_2O)_2][PF_6]_2{\cdot}H_2O$	1724	163
$[MnL^5(H_2O)_2][PF_6]_2{\cdot}H_2O$	1718	161
$[FeL^5(H_2O)_2][PF_6]_2{\cdot}H_2O$	1715	163
$[CoL^5][PF_6]_2{\cdot}H_2O$	1710	165
$[NiL^5(H_2O)_2][PF_6]_2{\cdot}MeCN$	1724	167
$[CuL^5(H_2O)_2][PF_6]_2{\cdot}H_2O$	1735	162
$[ZnL^5(H_2O)_2][PF_6]_2{\cdot}H_2O$	1725	161
$[MnL^6(H_2O)_2][PF_6]_2{\cdot}H_2O$	-	160
$[FeL^6(H_2O)_2][PF_6]_2{\cdot}H_2O$	-	162
$[CoL^6][PF_6]_2{\cdot}H_2O$	-	164
$[NiL^6(H_2O)_2][PF_6]_2{\cdot}MeCN$	-	165
$[CuL^6(H_2O)_2][PF_6]_2{\cdot}H_2O$	-	164
$[ZnL^6(H_2O)_2][PF_6]_2{\cdot}H_2O$	-	160

6. Conclusion

We have shown that derivatized planar pentadentate ligands may be prepared by esterification and functional group interconversions of suitable hydroxyethyl substituted macrocyclic ligand. These ligands appear to possess a coordination chemistry which parallels that of related unsubstituted ligand.

7. Aknowlegments

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