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Novel N_4 Macrocycles and Their Transition Metal Chelates

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ABSTRACT

Four novel N_4-type macrocyclic chelating agents L^1, L^2, L^3, L^4 with pendant groups and their metal chelates with some transition metal ions have been synthesized. Electrical conductance of the Cr(III) and Fe(III) chelates indicated them to be 1:1 electrolytes whilst those of divalent metal ions are non-electrolytes in DMSO. Spectroscopic evidence suggests that all of the complexes are six-coordinate and the pendant groups are not involved in coordination.

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INTRODUCTION

The coordination properties of macrocycle bearing pendant groups have attracted great deal of attention.[1−4] More recently, the crystal and molecular structure of [3-(4-pyridiniumcarbonyl)-1,3,5,8,12,-pentaazacyclotetradecane]-nickel(II) was described[5] in which pyridine acts as pendant group. A metallocyclam subunit has been appended to pyridine through a metal template procedure which involves the condensation of amides of 3- and 4-pyridine carboxylic acid with formaldehyde and the nickel(II) complex with the open-chain tetraamine. These metallocyclam units act as building blocks of supramolecular system and act as two-electron redox systems. In the recent past, a 36-membered macrocycle with four ethylenediamine entities has been reported.[6]

The synthesis of transition metal complexes with macrocycles containing a variety of functional groups on the periphery has been reported.[7] These groups have been termed superstructures. Such compounds are of particular importance in view of their use in the treatment of malignant tumors.[8] Increasing interest has been shown in the design of new macrocycles with predetermined guest complexation.[9,10] In view of these observations it was considered worthwhile to investigate, in detail, the synthesis of four tetradentate macrocycles and their chelates with transition metal ions.

RESULTS AND DISCUSSION

A mixture of 4-aminoantipyrine, acetylacetone and 1,3-diaminopropane or 1,6-diaminohexane was refluxed. It was cooled to zero °C and an excess of dilute HCl was added to cause precipitation of L^1 and L^2 as shown in Figure 1.

For the synthesis of L^3 and L^4, a mixture of 4-aminoantipyrine, 1,3-diaminopropane or ethylenediamine was refluxed for 20 h. It was cooled to zero °C and precipitated with dilute HCl. This product was dissolved in ethanol and refluxed with benzoylacetic acid. Addition of dilute HCl afforded the ligands L^3 and L^4 (Figure 2).

Metal complexes were synthesized directly by the addition of hydrated metal chloride solutions to the ligand solution in the same solvent. Since the yield of the complexes was too poor (10 to 15%), the in situ method was employed. In this method the ligand was not isolated. The metal chloride was added to the solution of the ligand under preparation.

Elemental analyses of the complexes correspond to the compositions $MLCl_2$ and $M'LCl_3$ where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) and

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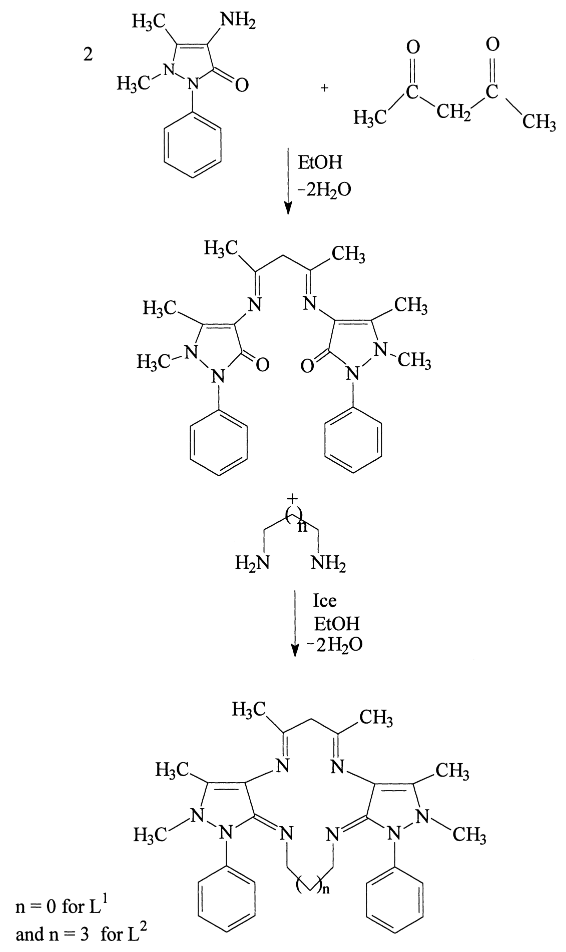

Figure 1. Synthesis of ligands L^1 and L^2.

M′ = Cr(III) and Fe(III). The molar conductances measured in DMSO (15–42 ohm^{-1} cm^2 mole^{-1}) indicated that the divalent metal complexes are non electrolytes[10] while those of M(III) ions are 1:1 electrolytes (Table 1).

IR Spectra

It has been observed by many workers[11,12] that in Schiff base macrocyclic complexes the C = N stretching frequency appears in the 1620–1660 cm^{-1} region. A comparison of the IR spectra of the free macrocycles

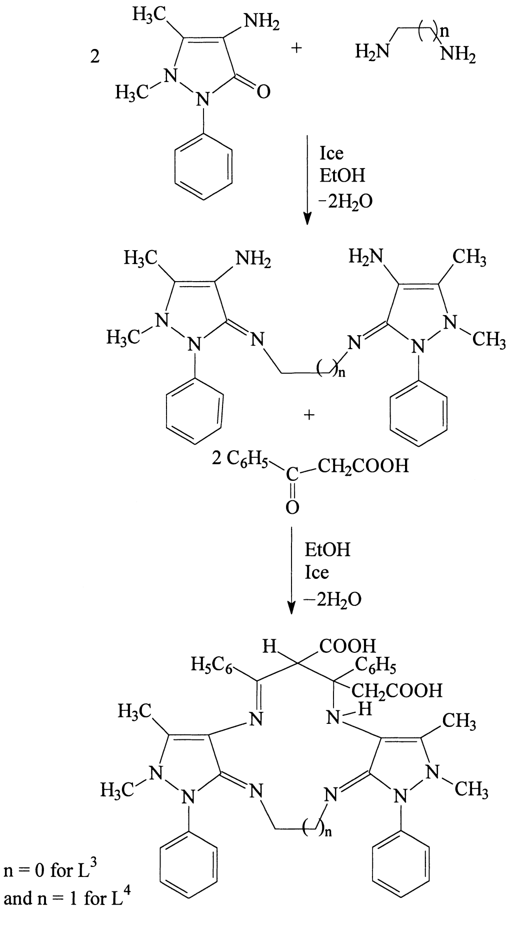

Figure 2. Synthesis of ligands L^3 and L^4.

with those of their complexes indicated a substantial shift in ν(C=N) and ν(C−N) (Table 2). The presence of ν(NH) in L^3 and L^4 and their complexes has been supported by the appearance of a band in the 3080–3230 cm^{-1} region. It is interesting to note that ν(COOH) consistently appears at 1430 cm^{-1} in both the free (L^3 and L^4) and chelated macrocycles which implies that the pendant group is not coordinated in any case although macrocycles having pendant donor groups that are capable of coordinating with the central metal ions are known.[13] Some 'scorpiand' type molecules are also reported having H_2N-CH_2 'tails' to a tetraamine macrocycle.[9]

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Table 1. Physical properties and analytical data for L^1, L^2, L^3, L^4 and its metal chelates.

	Compounds (formula weight)	Yield (%)	Color	M.p.[a] (°C)	Molar conductance (ohm^{-1} cm^2 mol^{-1})	% Analysis found (calcd).				
						C	H	N	CI	M
	L^1, $C_{30}H_{36}N_8$ (508.67)	20	Orange	200	–	70.5 (70.8)	7.2 (7.1)	22.1 (22.0)	–	–
(**1**)	$[CrL^1Cl_2]$ Cl-$C_{30}H_{36}Cl_3CrN_8$ (667.03)	40	Green	330 d	61	54.5 (54.0)	5.5 (5.4)	16.2 (16.8)	15.4 (15.9)	7.2 (7.8)
(**2**)	$[MnL^1Cl_2]$-$C_{30}H_{36}Cl_2MnN_8$ (634.51)	28	Brown	260 d	15	56.5 (56.8)	5.5 (5.7)	17.5 (17.7)	11.2 (11.1)	8.8 (8.6)
(**3**)	$[FeL^1Cl_2]$Cl-$C_{30}H_{36}Cl_3FeN_8$ (670.88)	35	Brown	265 d	71	53.3 (53.7)	5.0 (5.4)	16.4 (16.7)	15.5 (15.8)	8.6 (8.3)
(**4**)	$[CoL^1Cl_2]$-$C_{30}H_{36}Cl_2CoN_8$ (638.50)	38	Pink	280 d	26	56.9 (56.4)	5.9 (5.6)	17.2 (17.6)	11.2 (11.1)	9.7 (9.2)
(**5**)	$[NiL^1Cl_2]$-$C_{30}H_{36}Cl_2N_8Ni$ (638.28)	41	Green	295 d	30	56.1 (56.5)	5.1 (5.6)	17.2 (17.6)	11.5 (11.1)	9.5 (9.2)
(**6**)	$[CuL^1Cl_2]$-$C_{30}H_{36}Cl_2CuN_8$ (643.12)	39	Green	310 d	32	56.5 (56.0)	5.8 (5.6)	17.8 (17.4)	11.5 (11.0)	9.3 (9.8)

(*continued*)

Table 1. Continued.

	Compounds (formula weight)	Yield (%)	Color	M.p.[a] (°C)	Molar conductance (ohm^{-1} cm^2 mol^{-1})	% Analysis found (calcd)				
						C	H	N	CI	M
(**7**)	[ZnL^{1}Cl$_2$]- $C_{30}H_{36}Cl_2N_8Zn$ (644.95)	36	White	320 d	42	55.6 (55.9)	5.8 (5.6)	17.5 (17.3)	11.3 (11.0)	10.2 (10.1)
	L^2, $C_{33}H_{42}N_8$ (550.75)	25	Yellow	210	–	72.2 (71.9)	7.9 (7.7)	20.5 (20.3)	–	–
(**8**)	[CrL^{2}Cl$_2$]Cl- $C_{33}H_{42}Cl_3CrN_8$ (709.11)	36	Green	295 d	70	55.5 (55.9)	5.8 (5.9)	15.3 (15.8)	14.6 (15.0)	7.5 (7.3)
(**9**)	[MnL^{2}Cl$_2$]- $C_{33}H_{42}Cl_2MnN_8$ (676.59)	38	Grey	340 d	40	58.3 (58.6)	6.6 (6.3)	16.1 (16.6)	10.7 (10.5)	8.4 (8.1)
(**10**)	[FeL^{2}Cl$_2$]Cl- $C_{33}H_{42}Cl_3FeN_8$ (712.96)	41	Brown	320 d	53	55.2 (55.6)	5.7 (5.9)	15.4 (15.7)	14.5 (14.9)	7.5 (7.8)
(**11**)	[CoL^{2}Cl$_2$]- $C_{33}H_{42}Cl_2CoN_8$ (680.58)	43	Pink	340 d	34	58.5 (58.2)	6.1 (6.2)	16.7 (16.5)	16.9 (16.5)	8.9 (8.6)
(**12**)	[NiL^{2}Cl$_2$]- $C_{33}H_{42}Cl_2N_8Ni$ (680.36)	42	Green	330 d	27	57.8 (58.3)	6.5 (6.2)	16.9 (16.5)	10.8 (10.4)	8.9 (8.6)

(**13**)	$[CuL^2Cl_2]$- $C_{33}H_{42}Cl_2CuN_8$ (685.20)	45	Green	290	17	57.2 (57.8)	6.2 (6.2)	16.2 (16.4)	10.5 (10.4)	9.9 (9.3)
(**14**)	$[ZnL^2Cl_2]$- $C_{33}H_{42}Cl_2N_8$ Zn (687.03)	42	White	280 d	18	57.3 (57.7)	6.2 (6.2)	16.4 (16.3)	10.9 (10.3)	9.7 (9.5)
	L^3, $C_{42}H_{42}N_8O_4$ (722.85)	28	White	240	–	69.3 (69.8)	5.9 (5.8)	15.5 (15.5)	–	–
(**15**)	$[CrL^3Cl_2]Cl$- $C_{42}H_{42}Cl_3CrN_8O$ (881.21)	40	Green	257 d	70	57.5 (57.2)	4.9 (4.8)	12.8 (12.7)	12.2 (12.0)	5.4 (5.9)
(**16**)	$[MnL^3Cl_2]$- $C_{42}H_{42}Cl_2MnN_8O_4$ (848.69)	38	Grey	290 d	22	58.9 (59.4)	4.8 (2.9)	13.5 (13.2)	8.4 (8.3)	6.1 (6.4)
(**17**)	$[FeL^3Cl_2]Cl$ $C_{42}H_{42}Cl_3FeN_8O_4$ (885.06)	36	Brown	320 d	80	56.5 (56.9)	4.6 (4.7)	12.2 (12.6)	12.5 (12.0)	6.4 (6.3)
(**18**)	$[CoL^3Cl_2]$ $C_{42}H_{42}Cl_2CoN_8O_4$ (852.68)	28	Pink	340 d	28	59.2 (59.1)	4.7 (4.9)	13.5 (13.1)	8.5 (8.3)	6.5 (6.9)
(**19**)	$[NiL^3Cl_2]$ $C_{42}H_{42}Cl_2N_8$ NiO_4 (852.46)	29	Green	320 d	32	58.7 (59.1)	4.4 (4.9)	13.6 (13.5)	8.5 (8.3)	6.7 (6.9)
(**20**)	$[CuL^3Cl_2]$ $C_{42}H_{42}Cl_2CuN_8O_4$ (857.30)	32	Green	330 d	42	58.5 (58.8)	4.5 (4.9)	13.4 (13.0)	8.6 (8.2)	7.9 (7.4)

(*continued*)

Table 1. Continued.

	Compounds (formula weight)	Yield (%)	Color	M.p.[a] (°C)	Molar conductance (ohm^{-1} cm^2 mol^{-1})	% Analysis found (calcd)				
						C	H	N	CI	M
(**21**)	[ZnL^{3}Cl$_2$]- $C_{42}H_{42}Cl_2N_8O_4$ Zn (859.13)	33	White	350 d	40	58.2 (58.6)	4.4 (4.9)	13.3 (13.0)	7.8 (8.2)	7.6 (7.8)
	L^4, $C_{43}H_{44}$ N_8O_4 (736.87)	23	White	230	–	70.5 (70.0)	6.5 (6.0)	15.6 (15.2)	–	–
(**22**)	[CrL^{4}Cl$_2$]Cl- $C_{43}H_{44}Cl_3CrN_8O_4$ (895.23)	42	Green	265 d	52	58.1 (57.6)	4.6 (4.9)	12.2 (12.5)	11.3 (11.8)	5.6 (5.8)
(**23**)	[MnL^{4}Cl$_2$]- $C_{43}H_{44}Cl_2MnN_8O_4$ (862.71)	24	Grey	320 d	25	59.3 (59.8)	4.7 (5.1)	12.5 (13.0)	8.5 (8.2)	6.8 (6.3)
(**24**)	[FeL^{4}Cl$_2$]Cl- $C_{43}H_{44}Cl_3FeN_8O_4$ (899.01)	28	Brown	340 d	61	57.2 (57.5)	4.8 (4.9)	12.2 (12.5)	11.3 (11.8)	6.5 (6.2)

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(**25**)	$[CoL^4Cl_2]$- $C_{43}H_{44}Cl_2CoN_8O_4$ (866.70)	41	Pink	350 d	41	60.1 (59.6)	5.5 (5.1)	12.6 (12.9)	8.2 (8.1)	6.6 (6.8)
(**26**)	$[NiL^4Cl_2]$- $C_{43}H_{44}Cl_2N_8NiO_4$ (866.48)	29	Green	310 d	30	59.2 (59.6)	5.5 (5.1)	12.4 (12.9)	8.3 (8.1)	6.3 (6.7)
(**27**)	$[CuL^4Cl_2]$- $C_{43}H_{44}Cl_2CuN_8O_4$ (871.32)	26	Green	380 d	27	59.6 (59.2)	4.7 (5.0)	12.4 (12.8)	8.4 (8.1)	6.8 (7.3)
(**28**)	$[ZnL^4Cl_2]$ $C_{43}H_{44}Cl_2N_8O_4Zn$ (873.15)	28	White	290 d	28	59.2 (59.1)	5.4 (5.0)	12.5 (12.8)	8.3 (8.1)	7.0 (7.4)

[a] d = decomposition.

Table 2. Important IR bands (cm^{-1}) for ligands and their metal chelates.

	Compounds	ν(C = N)	ν(C–N)	ν(N–N)	ν(M–N)	ν(M–CI)
	L^1	1660 s	1410 w	1070 w	–	–
(**1**)	$[Cr(L^1)Cl_2]Cl$	1620 s	1380 w	1070 w	390 w	265 w
(**2**)	$[Mn(L^1)Cl_2]$	1630 s	1390 w	1070 w	330 w	270 w
(**3**)	$[Fe(L^1)Cl_2]Cl$	1640 s	1410 w	1070 w	340 w	285 w
(**4**)	$[Co(L^1)Cl_2]$	1620 s	1390 w	1070 w	340 w	285 w
(**5**)	$[Ni(L^1)Cl_2]$	1630 s	1380 w	1070 w	345 w	295 w
(**6**)	$[Cu(L^1)Cl_2]$	1640 s	1380 w	1070 w	335 w	295 w
(**7**)	$[Zn(L^1)Cl_2]$	1620 s	1370 w	1070 w	330 w	280 w
	L^2	1655 s	1070 m	1390 m	–	–
(**8**)	$[Cr(L^2)Cl_2]Cl$	1640 s	1070 m	1370 m	390 w	280 w
(**9**)	$[Mn(L^2)Cl_2]$	1630 s	1070 m	1360 m	330 w	285 w
(**10**)	$[Fe(L^2)Cl_2]Cl$	1645 s	1070 m	1375 m	380 w	260 w
(**11**)	$[Co(L^2)Cl_2]$	1635 s	1070 m	1380 m	320 w	265 w
(**12**)	$[Ni(L^2)Cl_2]$	1630 s	1070 m	1360 m	330 w	270 w
(**13**)	$[Cu(L^2)Cl_2]$	1620 s	1070 m	1370 m	340 w	260 w
(**14**)	$[Zn(L^2)Cl_2]$	1620 s	1070 m	1380 m	320 w	275 w

	L^3	3230 m	1660 s	1400 m	1420 m	1615 m	1070 w	–	–
(**15**)	$[Cr(L^3)Cl_2]Cl$	3200 m	1640 s	1380 m	1420 m	1615 m	1070 w	380 w	300 w
(**16**)	$[Mn(L^3)Cl_2]$	3210 m	1650 s	1360 m	1420 m	1615 m	1070 w	345 w	290 w
(**17**)	$[Fe(L^3)Cl_2]Cl]$	3220 m	2645 s	1380 m	1420 m	1615 m	1070 w	390 w	280 w
(**18**)	$[Co(L^3)Cl_2]$	3210 m	1640 s	1380 m	1420 m	1615 m	1070 w	335 w	260 w
(**19**)	$[Ni(L^3)Cl_2]$	3220 m	1640 s	1390 m	1410 m	1615 m	1070 w	340 w	255 w
(**20**)	$[Cu(L^3)Cl_2]$	3220 m	1630 s	1370 m	1410 m	1615 m	1070 w	345 w	265 w
(**21**)	$[Zn(L^3)Cl_2]$	3210 m	1650 s	1360 m	1420 m	1615 m	1070 w	345 w	270 w
	L^4	3100 m	1670 s	1480 m	1420 m	1615 m	1070 w	–	–
(**22**)	$[Cr(L^4)Cl_2]Cl$	3090 m	1660 s	1360 m	1420 m	1615 m	1070 w	385 w	290 w
(**23**)	$[Mn(L^4)Cl_2]$	3080 m	1640 s	1360 m	1420 m	1615 m	1070 w	330 w	295 w
(**24**)	$[Fe(L^4)Cl_2]Cl$	3090 m	1645 s	1365 m	1420 m	1615 m	1070 w	375 w	290 w
(**25**)	$[Co(L^4)Cl_2]$	3080 m	1650 s	1370 m	1410 m	1615 m	1070 w	320 w	280 w
(**26**)	$[Ni(L^4)Cl_2]$	3080 m	1650 s	1360 m	1420 m	1615 m	1070 w	340 w	285 w
(**27**)	$[Cu(L^4)Cl_2]$	3090 m	1655 s	1360 m	1420 m	1615 m	1070 w	320 w	280 w
(**28**)	$[Zn(L^4)Cl_2]$	3100 m	1650 s	1370 m	1420 m	1615 m	1070 w	340 w	295 w

Table 3. Magnetic susceptibility, electronic spectra, and ligand field parameters of the complexes.

	Compounds	Magnetic moment (B.M.)	Electronic bands (cm^{-1})	ε ($mol^{-1}cm^2$)	Possible assignments	10Dq (cm^{-1})	B (cm^{-1})	β
(**1**)	$[Cr(L^1)Cl_2]Cl$	3.80	35,714	20	$^4T_{1g}(P)\leftarrow{}^4A_{2g}(F)$	13400	900	0.87
			21,978	13	$^4T_{1g}(F)\leftarrow{}^4A_{2g}(F)$			
			15,151	9	$^4T_{2g}(F)\leftarrow{}^4A_{2g}(F)$			
(**2**)	$[Mn(L^1)Cl_2]$	5.99	25,974	16	$^4A_{1g}(G)\leftarrow{}^6A_{1g}$	10890	690	0.72
			23,255	13	$^4T_{2g}(G)\leftarrow{}^6A_{1g}$			
			17,241	11	$^4T_{1g}(G)\leftarrow{}^6A_{1g}$			
(**3**)	$[Fe(L^1)Cl_2]Cl$	5.88	33,333	24	$^4T_{1g}(P)\leftarrow{}^6A_{1g}$	12240	840	0.76
			28,985	17	$^4E_g(D)\leftarrow{}^6A_{1g}$			
			21,052	12	$^4T_{2g}(G)\leftarrow{}^6A_{1g}$			
(**4**)	$[Co(L^1)Cl_2]$	3.20	22,988	21	$^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$	11870	800	0.82
			18,018	16	$^4A_{2g}(F)\leftarrow{}^4T_{1g}(F)$			
			12,987	7	$^4T_{2g}(F)\leftarrow{}^4T_{1g}(F)$			
(**5**)	$[Ni(L^1)Cl_2]$	3.20	27,027	32	$^3T_{1g}(P)\leftarrow{}^3A_{2g}(F)$	11820	760	0.70
			23,809	24	$^3T_{1g}(F)\leftarrow{}^3A_{2g}(F)$			
			13,986	11	$^3T_{2g}(F)\leftarrow{}^3A_{2g}(F)$			
(**6**)	$[Cu(L^1)Cl_2]$	1.96	33,258	14	Charge transfer	13157	–	–
			13,157	9	$^2T_{2g}\leftarrow{}^2E_g$			
(**7**)	$[Zn(L^1)Cl_2]$	Diamagnetic						
(**8**)	$[Cr(L^2)Cl_2]Cl$	3.88	34,482	28	$^4T_{1g}(P)\leftarrow{}^4A_{2g}(F)$	11090	880	0.85
			25,000	21	$^4T_{1g}(F)\leftarrow{}^4A_{2g}(F)$			
			18,000	17	$^4T_{2g}(F)\leftarrow{}^4A_{2g}(F)$			

(**9**)	$[Mn(L^2)Cl_2$	6.12	33,333	22	${}^4T_{1g}(P) \leftarrow {}^6A_{1g}$	8010	620	0.65
			21,052	18	${}^4T_{1g}(G) \leftarrow {}^6A_{1g}$			
			17,241	9	${}^4T_{1g}(G) \leftarrow {}^6A_{1g}$			
(**10**)	$[Fe(L^2)Cl_2]Cl$	5.89	32,258	32	${}^4T_{1g}(P) \leftarrow {}^6A_{1g}(F)$	11210	840	0.76
			22,988	27	${}^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$			
			18,000	21	${}^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$			
(**11**)	$[Co(L^2)Cl_2]$	4.60	22,988	18	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	10860	720	0.74
			19,047	15	${}^4A_{2g}(F) \leftarrow {}^4T_{2g}(F)$			
			12,048	11	${}^4T_{1g}(F) \leftarrow {}^4T_{2g}(F)$			
(**12**)	$[Ni(L^2)Cl_2]$	3.32	25,974	30	${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	9990	710	0.66
			16,000	23	${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$			
			11,111	17	${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$			
(**13**)	$[Cu(L^2)Cl_2]$	1.93	28,571	20	charge transfer	11235	–	–
			11,235	13	${}^2T_{2g} \leftarrow {}^2E_g$			
(**14**)	$[Zn(L^2)Cl_2]$	Diamagnetic						
(**15**)	$[Cr(L^3)Cl_2]Cl$	3.88	34,482	12	${}^4T_{1g}(P) \leftarrow {}^4A_{2g}(F)$	13200	900	0.87
			20,000	8	${}^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$			
			16,949	5	${}^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$			
(**16**)	$[Mn(L^3)Cl_2]$	6.04	32,258	30	${}^4A_{1g}(G) \leftarrow {}^6A_{1g}$	9990	670	0.70
			22,727	27	${}^4T_{2g}(G) \leftarrow {}^6A_{1g}$			
			16,666	22	${}^4T_{1g}(G) \leftarrow {}^6A_{1g}$			
(**17**)	$[Fe(L^3)Cl_2]Cl$	6.01	30,303	28	${}^4E_g(D) \leftarrow {}^6A_{1g}$	12210	860	0.78
			23,255	23	${}^4T_{2g}(G) \leftarrow {}^6A_{1g}$			
			18,000	19	${}^4T_{1g}(G) \leftarrow {}^6A_{1g}$			
(**18**)	$[Co(L^3)Cl_2]$	3.30	21,978	18	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	11820	790	0.81
			18,018	15	${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$			
			12,987	7	${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$			

(*continued*)

Table 3. Continued.

	Compounds	Magnetic moment (B.M.)	Electronic bands (cm^{-1})	ε ($mol^{-1}cm^2$)	Possible assignments	10Dq (cm^{-1})	B (cm^{-1})	β
(**19**)	$[Ni(L^3)Cl_2]$	3.21	25,974	34	$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	10860	740	0.69
			22,988	29	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$			
			13,986	21	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$			
(**20**)	$[Cu(L^3)Cl_2]$	1.99	30,303	24	Charge transfer	12987	–	–
			12,987	12	$^2T_{2g} \leftarrow {}^2E_g$			
(**21**)	$[Zn(L^3)Cl_2]$	Diamagnetic				–	–	–
(**22**)	$[Cr(L^4)Cl_2]Cl$	3.83	37,037	24	$^4T_{1g}(P) \leftarrow {}^4A_{2g}(F)$	14200	920	0.89
			19,047	17	$^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$			
			16,000	9	$^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$			
(**23**)	$[Mn(L^4)Cl_2]$	5.98	32,258	12	$^4T_{1g}(G) \leftarrow {}^6A_{1g}$	10320	710	0.74
			21,978	8	$^4T_{2g}(G) \leftarrow {}^6A_{1g}$			
			18,018	6	$^4T_{1g}(G) \leftarrow {}^6A_{1g}$			

(**24**)	$[Fe(L^4)Cl_2]Cl$	6.02	33,333	18	$^4T_{1g}(P) \leftarrow {}^6A_{1g}$	13320	890	0.81
			22,988	12	$^4T_{1g}(G) \leftarrow {}^6A_{1g}$			
			17,241	8	$^4T_{1g}(G) \leftarrow {}^6A_{1g}$			
(**25**)	$[Co(L^4)Cl_2]$	2.92	21,052	12	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	12210	820	0.85
			19,047	9	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$			
			10,989	7	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$			
(**26**)	$[Ni(L^4)Cl_2]$	3.22	27,777	30	$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	11880	780	0.72
			24,096	21	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$			
			13,986	15	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$			
(**27**)	$[Cu(L^4)Cl_2]$	1.98	34,482	36	Charge transfer	12987	–	–
			32,051	30	$^2T_{2g} \leftarrow {}^2E_g$			
			12,987	24				
(**28**)	$[Zn(L^4)Cl_2]$	Diamagnetic		–		–	–	–

The far IR spectra of the complexes show intense halogen-sensitive absorptions in the 255–300 cm^{-1} region. The bands in the 320–390 cm^{-1} range are assigned to ν(M–N) vibrations. A band at 1070 cm^{-1} in all the ligands and complexes is assigned to ν(N–N) in pyrazole.

Electronic Spectra and Magnetic Moments

The magnetic moment values and electronic spectral bands are given in Table 3. Three bands characteristic of octahedral nickel(II) ion in a high-spin state are anticipated. In the present case the bands observed have been assigned to $^3T_{2g}(P) \leftarrow {}^3A_{2g}(F)$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ transitions.[14] The electronic spectral bands and the relatively low magnetic moments suggest a distorted octahedral geometry for nickel(II) ion.

In all of the cobalt(II) complexes three bands have been observed. The magnetic moment value of Co(II) complexes with L^1, L^3 and L^4 is very low which is probably due to an equilibrium between low and high spin states of Co(II). However, the electronic bands and the pink colour of the complexes are consistent with an octahedral environment around cobalt(II) ion (Figure 3).

The observed magnetic moment values for chromium(III) complexes are close to that calculated for a d^3 ion, corresponding to an octahedral geometry (Figure 4).

The magnetic moment for all of the manganese(II) complexes ranges between 5.98–6.12 B.M. which correspond to a high-spin octahedral structure for the metal ion.[15]

The iron(III) complexes exhibit three bands. In the high-spin complexes the theoretical magnetic moment value is 5.91 B.M. We have obtained for these complexes values in the range for a high-spin octahedral geometry.[16]

The copper(II) complexes show one or two charge transfer bands. The band exhibited in the 11,235 – 13,157 cm^{-1} region is assigned to the $^2T_{2g} \leftarrow {}^2E_g$ transition which is characteristic of an octahedral copper(II) ion. The magnetic moment value also supports the above geometry.

EXPERIMENTAL

4-Aminoantipyrine, ethylenediamine, 1,3-diaminopropane, 1.6-diaminohexane (Koch Light) ethyl acetoacetate (S.D. Fine chemicals), acetylaczetone, benzoylchloride, and hydrated metal chlorides (BDH) were used as received. Benzoylacetic acid was synthesized and recrystallized by the literature method.[17] Elemental analyses were carried out with a Carlo Erba 1106 analyser. The metals were determined by complexometric titration[18] using EDTA and CI was determined gravimetrically.[19] The IR spectra ($4000-200\ \mathrm{cm}^{-1}$) were recorded on a 621 Perkin–Elmer grating spectrometer as KBr disc. The electronic spectra were recorded in DMSO on a Carl–Zeiss VSU2P spectrophotometer. Magnetic susceptibility measurements were done with an Allied Research model 155 vibrating sample magnetometer and the molar conductances were measured at room temperature using a Systronics 321 conductivity bridge.

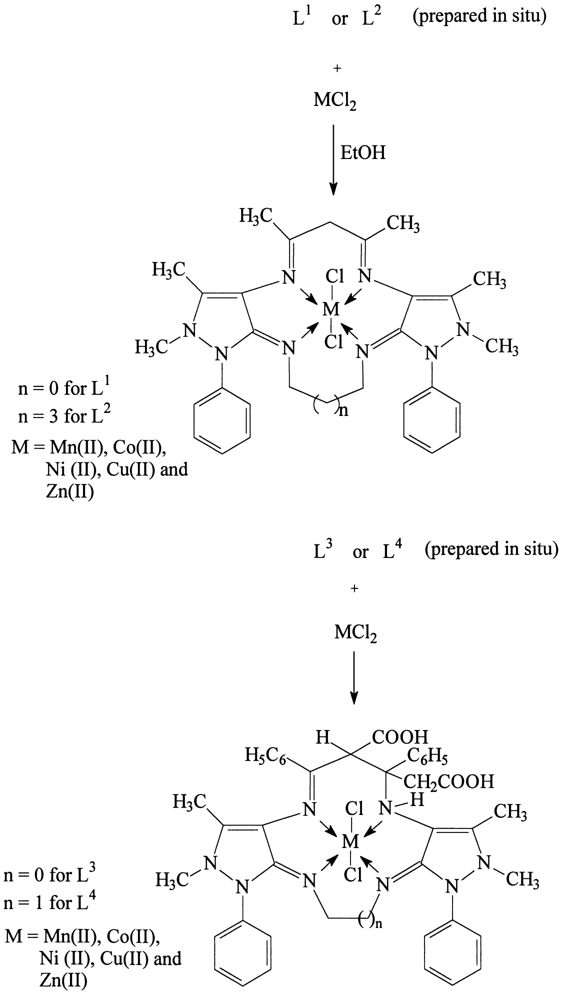

Figure 3. Synthesis of complexes of ligands L^1, L^2, L^3 and L^4.

Synthesis of L^1 and L^2

To a solution of 4-aminoantipyrine (20 mmol, 4.06 g) dissolved in 100 mL of hot ethanol, acetylacetone (10 mmol, 1.03 mL) was added and the mixture refluxed for half an hour in a round bottom flask. On cooling this mixture to room temperature, a light-orange precipitate was obtained

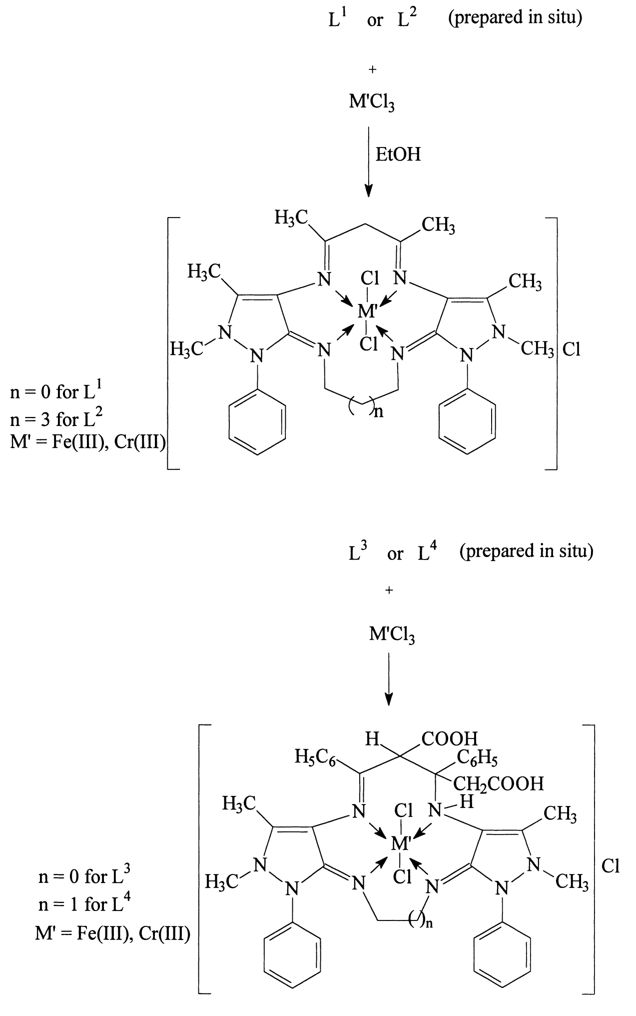

Figure 4. Synthesis of complexes of ligands L^1, L^2, L^3 and L^4.

(Figure 1). It was redissolved in THF (100 mL) and 1,6-diaminohexane (10 mmol, 1.16 g) or 1,3-diaminopropane (10 mmol, 0.85 mL) were then added and the mixture was refluxed for about 10 h. It was then cooled to 0 °C and an excess of 0.1 molar HCl (20 mL) was added to cause precipitation. The product was thoroughly washed with diethyl ether and dried in vacuo. Yield 1.27 g for L^1 (25%) and 1.48 g for L^2 (27%).

Synthesis of L^3 and L^4

A mixture of 4-aminoantipyrine (20 mmol, 4.06 g) and 1,3-diaminopropane (10 mmol, 0.85 mL) or ethylenediamine (10 mmol, 0.66 mL) in 100 mL ethanol was refluxed for about 20 h. It was cooled to 0 °C and acidified with 20 mL of 0.1 molar HCI which afforded a brown product. It was redissolved in hot ethanol (100 mL) and benzoylacetic acid (20 mmol, 3.2 g) was added to it .It was further refluxed for about 30 h and then cooled to 0 °C followed by the addition of 0.1 molar (20 mL) HCl which yielded a precipitate (Figure 2). It was washed thoroughly with ethanol and dried in vacuo. Yield 1.81 g for L^3 (25%) and 1.7 g for L^4 (23%).

General Methods for the Synthesis of Complexes

Initially we tried to synthesize the complexes by adding the metal salts to ligand solution, however the yields were poor (10 to 15%). To overcome this problem, the complexes were synthesized in situ, in which salts were immediately added to the solution of ligand under preparation (Figures 3 and 4).

Acetylacetone (2 mmol, 0. 20 mL) was added drop-wise to an ethanolic solution (50 mL) of 4-aminoantipyrine (4 mmol, 0.80 g). After refluxing this mixture for about half an hour 1,6-diaminohexane (2 mmol, 0.23 g) was added and further refluxed for 24 h. The mixture was then cooled to 0 °C and hydrated metal chloride (2 mmol) in ethanol (25 mL) was added which afforded brisk precipitation of coloured complexes. It was filtered, washed with cold ethanol and dried in vacuo.

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