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Chelating Behavior of 14-Membered Schiff Base Macrocycles and Their Transition Metal Chelates

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Chelating Behavior of 14-Membered Schiff Base Macrocycles and Their Transition Metal Chelates

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ABSTRACT

The new Schiff base 14-membered macrocycles, 1,5,8,12-tetraazacyclotetradeca-6,7,13,14-tetraaminoacetic acid-5,7,12,14-tetraene (L^1), 1,5,8,12-tetraazacyclotetradeca-6,7,13,14-tetraaminophenyl-5,7,12,14tetraene (L^2) and 1,5,8,12-tetraazacyclotetradeca-6,7,13,14-tetraaminopyridyl-5,7,12,14-tetraene (L^3), have been synthesized by the reaction of N,N-dicarboxymethyloxamide, N,N-diphenyloxamide or N,Ndipyridyloxamide with 1,3-diaminopropane. Their complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions have been prepared and characterized by elemental analyses, IR, ¹H NMR and electronic spectra, magnetic moment and conductivity measurements.

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The complexes of the divalent metal ions are non-ionic while those of the trivalent metal ions appear to be 1:1 electrolytes. On the basis of these studies an octahedral geometry is proposed for all of the complexes.

Key Words: 14-Membered macrocycles; Schiff base; Synthesis; Metal chelates.

INTRODUCTION

The design and synthesis of macrocycles and their metal chelates is a subject of current research interest.^[1-6] A great deal of interest has been directed to metal complexes with functionalized macrocycles that have pendant functional groups.^[7-9] The chemistry of macrocycles has aroused increasing interest in recent years due to their use as models for protein metal binding sites in metalloproteins, as therapeutic reagents in chelate therapy for the treatment of metal intoxication, in catalysis and in the treatment of cancer.^[10-12]

In this paper we report the synthesis and characterization of the 14membered N_4 macrocycles L^1 , L^2 and L^3 and their complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions.

RESULTS AND DISCUSSION

The ligands were synthesized according to the scheme in Fig. 1. The complexes were synthesized by heating over a water bath for 6 h a 1:1 mixture of hydrated metal chloride dissolved in methanol and ligand in ethanol and an aqueous buffer of pH 4, which afforded a precipitate. It was washed with ethanol and dried over CaCl₂. The molar conductances of one millimolar solutions in DMSO showed that the complexes of the divalent metal ions are non-electrolytes while those of the trivalent metal ions appear to be 1:1 electrolytes^[13] (Tables 1–3).

 $MCl_2 + L \longrightarrow [MLCl_2]$ $MCl_3 + L \longrightarrow [MLCl_2]Cl$

where $L = L^1$, L^2 and L^3 .

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Figure 1. Synthesis of the ligands.

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 (L^2)

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IR Spectra

The relevant IR bands and their assignments are listed in Tables 4–6. The two $\nu(C=0)$ bands appearing at 1710 and 1640 cm⁻¹ in N,N-dicarboxymethyloxamide are lost and $\nu(C=N)$ (1670 cm⁻¹) appears, as a consequence of its reaction with 1,3-diaminopropane forming a macrocyclic Schiff base (Fig. 1). In the present work we have observed only one band in the 1670–1690 cm⁻¹ in the free Schiff base macrocycles which undergoes a shift to lower wave number after chelation. This decrease in $\nu(C=N)$ in the complexes has been attributed to the coordination of the metal ion *via* nitrogen atoms.

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Table 1.

				Molar		Analy	sis found (calo	d.), %	
Compounds (formula weight)	Yield (%)	Colour	M.p. (°C)	$conductance (ohm^{-1} cm^2 mol^{-1})$	C	Н	Z	CI	Μ
C ₁₈ H ₂₈ N ₈ O ₈ (L ¹) (484.47)	30	White	138		44.22 (44.63)	5.69 (5.83)	23.01 (23.13)	I	I
[CrL ¹ Cl]Cl C ₁₈ H ₂₈ Cl ₃ CrN ₈ O ₈ (6/3 82)	40	Green	290 d	76	33.22 (33.64)	4.43 (4.39)	17.32 (17.44)	16.49 (16.55)	8.01 (8.08)
(072.02) [MnL ¹ Cl ₂] C ₁₈ H ₂₈ Cl ₂ MnN ₈ O ₈ (610.31)	38	Grey	320 d	25	35.86 (35.43)	4.39 (4.62)	18.73 (18.36)	11.43 (11.62)	(00.6) 66.6
(FeL ¹ Cl ₂) [FeL ¹ Cl ₂]Cl C ₁₈ H ₂₈ Cl ₃ FeN ₈ O ₈ (646.67)	39	Brown	330 d	103	33.32 (33.40)	4.89 (4.36)	17.01 (17.33)	16.55 (16.45)	8.29 (8.64)
[CoL ¹ Cl ₂] C ₁₈ H ₂₈ Cl ₂ CoN ₈ O ₈ (614.30)	46	Pink	325 d	20	35.63 (35.20)	4.93 (4.60)	18.10 (18.24)	11.87 (11.54)	9.82 (9.60)
[NiL ¹ Cl ₂] C ₁₈ H ₂₈ Cl ₂ N ₆ NiO ₆ (614.08)	42	Green	310 d	18	35.72 (35.21)	4.88 (4.60)	18.39 (18.25)	11.67 (11.56)	9.67 (9.56)
[CuL ¹ Cl ₂] C ₁₈ H ₂₈ Cl ₂ CuN ₈ O ₈ (618.91)	41	Green	290 d	27	34.62 (34.93)	4.62 (4.56)	18.21 (18.10)	11.56 (11.46)	10.53 (10.27)
$[ZnL^{1}Cl_{2}]$ $C_{18}H_{28}Cl_{2}N_{8}O_{8}Zn$ (620.74)	32	White	285 d	30	34.22 (34.83)	4.67 (4.55)	18.23 (18.05)	11.55 (11.42)	10.66 (10.53)

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	Table 2	. Physic	al propert	ies and analy	tical data of L ²	and its meta	l chelates.		
				Molar		Analys	sis found (calcd.)	% (
Compounds (formula weight)	Yield (%)	Colour	M.p. (°C)	$\begin{array}{c} \text{conductance} \\ (\text{ohm}^{-1} \\ \text{cm}^2 \text{mol}^{-1}) \end{array}$	U	Н	z	G	Μ
C ₃₄ H ₃₆ N ₈ (L ²) (556.71) [CrL ² Cl ₂]Cl C ₃₄ H ₃₆ Cl ₂ CrN ₈	26 33	White Green	145 279 d	— 110	73.86 (73.35) 57.26 (57.11)	6.22 (6.52) 5.71 (5.07)	20.20 (20.13) 15.51 (15.67)	— 14.93 (14.87)	7.16 (7.27)
(715.07) [MnL ² Cl ₂] C ₃₄ H ₃₆ Cl ₂ MnN ₈ (250.55)	42	Brown	280 d	35	59.35 (59.83)	5.12 (5.32)	16.59 (16.42)	10.56 (10.39)	8.23 (8.05)
(100220) [FeL ² Cl ₂]Cl C ₃₄ H ₃₆ Cl ₃ FeN ₈ (718.02)	36	Brown	330 d	76	56.72 (56.80)	5.15 (5.05)	15.72 (15.59)	14.91 (14.80)	7.36 (7.77)
[CoL ² Cl ₂] C ₃₄ H ₃₆ Cl ₂ CoN ₈	35	Pink	310 d	42	59.71 (59.48)	5.19 (5.29)	16.12 (16.32)	10.51 (10.33)	8.63 (8.58)
(cc.000) [NiL ² Cl ₂] C ₃₄ H ₃₆ Cl ₂ N ₈ Ni (686 33)	42	Light	275 d	40	59.42 (59.50)	5.31 (5.25)	16.23 (16.33)	10.54 (10.33)	8.71 (8.55)
$[CuL^2Cl_2] C_{34}H_{36}Cl_2CuN_8$ (601-16)	38	Sky	310 d	30	59.21 (59.08)	5.13 (5.25)	16.31 (16.21)	10.18 (10.26)	9.29 (9.19)
(021.10) [ZnL ² Cl ₂] C ₃₄ H ₃₆ Cl ₂ N ₈ Zn (692.99)	33	White	295 d	38	58.79 (58.93)	5.19 (5.24)	16.22 (16.17)	10.12 (10.23)	9.41 (9.43)

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		Table 3.	Physical p	roperties and an	alytical data of	L ³ and its me	stal chelates.	
				Molar		Anal	ysis found (calcd.	% (
nds 1 weight)	Yield (%)	Colour	M.p. (°C)	conductance $(ohm^{-1}$ $cm^2 mol^{-1})$	U	Н	z	G
$I_{12}(L^3)$	22	White	126		64.56 (64.27)	5.82 (5.75)	29.72 (29.97)	
	35	Green	300 d	120	50.23 (50.11)	4.59 (4.49)	23.43 (23.38)	14.86 (1

		Table 3.	Physical p	roperties and an	alytical data of	L' and its me	tal chelates.		
				Molar		Anal	/sis found (calcd.	% (
Compounds (formula weight)	Yield (%)	Colour	M.p. (°C)	conductance (ohm-1) cm2 mol-1)	C	Н	Z	G	М
$C_{30}H_{32}N_{12}$ (L ³)	22	White	126	1	64.56 (64.27)	5.82 (5.75)	29.72 (29.97)		
(560.67) [CrL ³ Cl ₂]Cl C ₃₀ H ₃₂ Cl ₃ Cl _{N12}	35	Green	300 d	120	50.23 (50.11)	4.59 (4.49)	23.43 (23.38)	14.86 (14.79)	7.19 (7.23)
(719.02) [MnL ³ Cl ₂] C ₃₀ H ₃₂ Cl ₂ MnN ₁₂	42	Grey	320 d	32	52.51 (52.49)	4.81 (4.48)	24.56 (23.48)	10.52 (10.33)	8.23 (8.00)
(682.56) [FeL ³ Cl ₂]Cl C ₃₀ H ₃₂ Cl ₃ FeN ₁₂	38	Brown	290 d	136	49.29 (49.85)	4.59 (4.46)	23.12 (23.25)	14.51 (14.71)	7.62 (7.73)
(722.87) [CoL ³ Cl ₂] C ₃₀ H ₃₂ Cl ₂ CoN ₁₂	32	Pink	300 d	43	52.22 (52.18)	4.52 (4.67)	24.22 (24.34)	10.38 (10.27)	8.66 (8.53)
(690.50) [NiL ³ Cl ₂] $C_{30}H_{32}Cl_2N_{12}N$	36	Light blue	320 d	40	52.31 (52.20)	4.59 (4.67)	24.30 (24.34)	10.32 (10.27)	8.62 (8.50)
(690.28) [CuL ³ Cl ₂] C ₃₀ H ₃₂ Cl ₂ CuN ₁₂	38	Sky blue	315 d	22	51.29 (51.84)	4.51 (4.64)	24.23 (24.18)	10.31 (10.20)	9.21 (9.14)
(695.11) [ZnL $^{3}Cl_{2}$] C $_{30}H_{32}Cl_{2}N_{12}Zn$ (696.94)	48	White	330 d	26	51.59 (51.70)	4.71 (4.63)	24.21 (24.12)	10.23 (10.17)	9.30 (9.38)
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Table 4. Important IR bands (cm^{-1}) of L^1 and its metal chelates.

Compounds	$\nu(\rm NH)$	$\nu(C=N)$	$\nu_{s}(\text{COOH})$	$\nu_{as}(COOH)$	$\nu(M-N)$	$\nu(M-Cl)$
L ¹	3,350 s	1,680 s	1,410 w	1,615 w		
[CrL ¹ Cl ₂]Cl	3,350 s	1,655 s	1,410 w	1,615 w	490 m	330 w
$[MnL^1Cl_2]$	3,350 s	1,640 m	1,410 w	1,615 w	460 m	350 w
[FeL ¹ Cl ₂]Cl	3,350 s	1,660 m	1,410 w	1,615 w	470 m	340 w
$[CoL^1Cl_2]$	3,350 s	1,670 m	1,410 w	1,615 w	480 m	342 w
$[NiL^2Cl_2]$	3,350 s	1,665 m	1,410 w	1,615 w	470 m	350 w
$[CuL^2Cl_2]$	3,350 s	1,665-m	1,410 w	1,615 w	470 m	345 w
$[ZnL^1Cl_2]$	3,350 s	1,665 m	1,410 w	1,615 w	490 m	370 w

The complexes exhibited new bands in the far-IR spectral region. The chromium(III) complexes show vibrational modes in the 490–510 cm⁻¹ range which are assigned to (Cr–N) stretches. The other metal ions exhibit M–N stretches in the 420–495 cm⁻¹ range. The ν (M–Cl) band has been found to appear in the 310–370 cm⁻¹ range. It is apparent from the spectra that both the nitrogen and chlorine are bonded to the metal ion.

In the case of metal complexes of L^1 nitrogen and oxygen of the pendant groups are not coordinated and hence their absorption bands remain unchanged throughout (Table 4). Similarly in the case of L^2 and L^3 the pendant arms have not been found to be involved in coordination which is evident from their spectra (Tables 5 and 6).

¹H NMR Spectra

The ligands L^1 , L^2 and L^3 show a triplet for the CH₂ protons at $\delta 2.7-2.9$, which shows a downfield shift in the complexes as given in Table 7.

Table 5. Important IR bands (cm^{-1}) of L^2 and its metal chelates.

Compounds	$\nu(NH)$	ν(C==N)	$\nu(C=C)$	ν (C–H)	$\nu(M-N)$	v(M-Cl)
L^2	3,230 s	1,670 s	1,580 w	2,940 w		
[CrL ² Cl ₂]Cl	3,230 s	1,645 m	1,580 w	2,955 w	495 m	330 w
$[MnL^2Cl_2]$	3,230 s	1,650 m	1,580 w	2,950 w	475 m	345 w
[FeL ² Cl ₂]Cl	3,230 s	1,655 m	1,580 w	2,960 m	420 m	340 w
$[CoL^2Cl_2]$	3,230 s	1,630 m	1,570 w	2,980 m	480 m	350 w
[NiL ² Cl ₂]	3,230 s	1,625 m	1,575 w	2,960 m	475 m	340 w
$[CuL^2Cl_2]$	3,230 s	1,620 m	1,580 w	2,960 m	485 m	310 w
$[ZnL^2Cl_2]$	3,230 s	1,665 m	1,570 w	2,980 m	485 m	320 w

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Compounds	ν(N-H)	ν(C=N)	ν(C=C)	Pyridine ring vibration	ν(M-N)	v(M-Cl)
L ³	3,250 s	1,675 m	1,580 w	1,615 m		
[CrL ³ Cl ₂]Cl	3,250 s	1,660 m	1,580 w	1,625 m	510 m	335 w
$[MnL^{3}Cl_{2}]$	3,250 s	1,640 m	1,580 w	1,625 m	495 m	340 w
[FeL ³ Cl ₂]Cl	3,250 s	1,655 m	1,580 w	1,620 m	470 m	350 w
$[CoL^{3}Cl_{2}]$	3,250 s	1,650 m	1,580 w	1,615 m	480 m	340 w
[NiL ³ Cl ₂]	3,250 s	1,650 m	1,580 w	1,625 m	495 m	330 w
$[CuL^{3}Cl_{2}]$	3,250 s	1,650 m	1,580 w	1,620 m	465 m	350 w
$[ZnL^{3}Cl_{2}]$	3,250 s	1,650 m	1,580 w	1,625 m	480 m	350 w

Table 6. Important IR bands (cm^{-1}) of L^3 and its metal chelates.

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The pendant group containing the moiety $CH_2CO_2H(L^1)$ exhibits a combined singlet for all of the methylene protons which is not influenced after metallation.^[14] The phenyl proton signal in N,N-diphenyloxamide (L²) exhibits multiplets at δ 6.5–6.8 while L³ shows multiplets due to pyridyl protons at δ 6.8–7.2. Since these pendant groups, both in the free and chelated macrocycles, did not show any change in the position of their proton signals, it is ascertained that they are not involved in coordination.

Electronic Spectra and Magnetic Moments

The magnetic moment values and electronic spectral bands are given in Tables 8–10. Three characteristic bands are anticipated for octahedral Ni(II) ion in the high-spin state. In the present case three bands observed at 23,255–25,000 cm⁻¹, 16,000–17,241 cm⁻¹ and 12,048–13,157 cm⁻¹ have been assigned to ${}^{3}T_{2g}(F) \leftarrow {}^{3}A_{2g}(F)$, ${}^{3}T_{1g}(F) \leftarrow {}^{2}A_{2g}(F)$ and ${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F)$ transitions, respectively. The relatively low magnetic moment values and the electronic spectral bands suggest a distorted octahedral geometry for the nickel(II) ion (Fig. 2).

In all Co(II) complexes three bands have been observed. The slightly low magnetic moment value for the complex of L^1 (4.4 B.M.) is attributed to the thermal depopulation of an excited quartet spin state which may be tentatively ascribed to the increasing size of the pendant groups. However, the electronic bands and the pink colour of the complexes are consistent with an octahedral environment around Co(II) ion.

The magnetic moments for the Cr(III), Fe(III) and Mn(II) complexes correspond to spin-free octahedral structures for the metal ion.^[15,16]



	Table	7. ¹ H NM	R of the li	gands and their Ni	(II) complexe	es.		
Compounds	β (NH)	δ (CH ₂)	J (Hz)	δ (CH ₂) of CH ₂ COOH	δ (COOH)	δ (C ₆ H ₅)	J (Hz)	δ (C ₅ H ₄ N)
N,N-Dicarboxymethyloxamide macrocycle (I, ¹)	7.8 (s)	2.75 (t) 2.22 (d)	7.8 6.5	4.2 (s)	11.2 (s)			
[NiL ¹ Cl ₂]	7.8 (s)	3.10 (t) 2.92 (q)	7.4 6.4	4.2 (s)	11.2 (s)			
N,N-Diphenyloxamide macrocycle (I ²)	7.2 (s)	2.8 (t) 2.31 (d)	7.0 7.3	I		6.5-6.8 (m)	9.0	
[NiL ² Cl ₂]	7.2 (s)	3.30 (t) 2.98 (q)	6.9 7.1	l		6.5-6.8 (m)	9.2	
N,N-Dipyridyloxamide macrowele (I ³)	7.1 (s)	2.90 (t) 2.52 (a)	7.1 7.6					6.8-7.2 (m)
[NiL ³ Cl ₂]	7.1 (s)	2.74 (q)	7.2 7.6	I				6.8-7.2 (m)





	Tab	ble 8. Magnetic n	noments and elec	ctronic spectra of the complex	es of L ¹ .		
Compounds	Magnetic moment (B.M.)	Electronic bands (cm ⁻¹)	$\log \varepsilon$ (L mol ⁻¹ cm ⁻¹)	Possible assignments	10 Dq (cm ⁻¹)	${f B}\ ({ m cm}^{-1})$	β
[CrL ¹ Cl ₂]Cl	3.85	36,000 26,315 18,018	1.52	$\begin{array}{l} {}^{4}T_{1g}(P) \longleftarrow {}^{4}A_{2g}(F) \\ {}^{4}T_{1g}(F) \longleftarrow {}^{4}A_{2g}(F) \\ {}^{4}T_{1g}(F) \longleftarrow {}^{4}A_{2g}(F) \\ {}^{4}T_{1g}(F) \longleftarrow {}^{4}A_{2g}(F) \end{array}$	13,660	1,040	1.00
[MnL ¹ Cl ₂]	6.00	30,303 28,571 24,096 19,000	1.68	$ \begin{array}{l} {}^{4}T_{1g}(P) \leftarrow {}^{6}A_{1g} \\ {}^{4}T_{2g}(D) \leftarrow {}^{6}A_{1g} \\ {}^{4}E_{g}(G) \leftarrow {}^{6}A_{1g} \\ {}^{4}T_{1g}(G) \leftarrow {}^{6}A_{1g} \\ \end{array} $	8,110	720	0.75
[FeL ¹ Cl ₂]Cl	5.97	37,037 28,985 24.390	1.71	Charge transfer ${}^{4}E_{g}(D) \leftarrow {}^{6}A_{1g}$ ${}^{4}A_{1,c}(G) \leftarrow {}^{6}A_{1,c}$	11,220	980	0.89
[CoL ¹ Cl ₂]	4.40	21,978 18,018 12,048	1.66	$ \begin{array}{c} {}^{4}\mathrm{T}_{1g}(\mathrm{P}) \leftarrow {}^{4}\mathrm{T}_{1g}(\mathrm{F}) \\ {}^{4}\mathrm{A}_{2g}(\mathrm{F}) \leftarrow {}^{4}\mathrm{T}_{1g}(\mathrm{F}) \\ {}^{4}\mathrm{T}_{2} \ \ (\mathrm{F}) \leftarrow {}^{4}\mathrm{A}_{1} \ \ (\mathrm{F}) \end{array} $	9,810	780	0.80
[NiL ¹ Cl ₂]	3.30	23,809 16,000 12,048	1.62	$\begin{array}{c} {}^{1}T_{1g}(\mathbf{P}) \leftarrow {}^{3}T_{2g}(\mathbf{r}) \\ {}^{3}T_{1g}(\mathbf{P}) \leftarrow {}^{3}T_{2g}(\mathbf{F}) \\ {}^{3}T_{1g}(\mathbf{F}) \leftarrow {}^{3}A_{2g}(\mathbf{F}) \\ {}^{3}T_{2e}(\mathbf{F}) \leftarrow {}^{3}A_{2e}(\mathbf{F}) \end{array}$	10,200	820	0.76
[CuL ¹ Cl ₂]	1.98	25,000 16,000	I	Charge transfer ${}^{2}T_{2g} \leftarrow {}^{2}E_{g}$		I	

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	Tab	ile 9. Magnetic n	noments and elec	ctronic spectra of the complex	es of L ² .		
Compounds	Magnetic moment (B.M.)	Electronic bands (cm ⁻¹)	$\log \varepsilon \ (\mathrm{L mol}^{-1}) \ \mathrm{cm}^{-1})$	Possible assignments	10 Dq (cm ⁻¹)	\mathbf{B} (cm^{-1})	β
[CrL ² Cl ₂]Cl	3.80	34,482 23,809 19,047	1.8	$\begin{array}{l} {}^{4}T_{1g}(P) \longleftarrow {}^{4}A_{2g}(F) \\ {}^{4}T_{1g}(F) \longleftarrow {}^{4}A_{2g}(F) \\ {}^{4}T_{1g}(F) \longleftarrow {}^{4}A_{2g}(F) \\ \end{array}$	10,001	810	0.79
[MnL ² Cl ₂]	5.88	33,333 28,000 22,222	1.85	$\begin{array}{l} {}^{4}T_{1g}(P) \leftarrow {}^{6}A_{1g} \\ {}^{4}E_{g}(D) \leftarrow {}^{6}A_{1g} \\ {}^{4}T_{2g}(G) \leftarrow {}^{6}A_{1g} \end{array}$		680	0.70
[FeL ² Cl ₂]Cl	5.89	29,411 23,255 19,000	1.89	$\begin{array}{l} {}^{4}E_{g}(D) \leftarrow {}^{6}A_{1g} \\ {}^{4}T_{2g}(G) \leftarrow {}^{6}A_{1g} \\ {}^{4}T_{1g}(G) \leftarrow {}^{6}A_{1g} \end{array}$	12,000	800	0.73
[CoL ² Cl ₂]	4.52	21,739 18,248 12,820	1.50	$\begin{array}{l} {}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}(F) \\ {}^{4}A_{2g}(F) \leftarrow {}^{4}T_{1g}(F) \\ {}^{4}T_{2g}(F) \leftarrow {}^{4}T_{1g}(F) \end{array}$	12,000	720	0.74
[NiL ² Cl ₂]	3.32	23,255 16,129 12,500	1.84	$\begin{array}{l} {}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F) \\ {}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}(F) \\ {}^{3}T_{2g}(F) \leftarrow {}^{3}A_{2g}(F) \end{array}$	11,440	760	0.70
[CuL ² Cl ₂]	1.98	23,255 16,129	I	Charge transfer ${}^{2}T_{2g} \leftarrow {}^{2}E_{g}$			I







	Tabi	le 10. Magnetic r	noments and ele	ctronic spectra of the complex	tes of L ³ .		
Compounds	Magnetic moment (B.M.)	Electronic bands (cm ⁻¹)	$\frac{\log \varepsilon}{(\mathrm{L} \mathrm{mol}^{-1})}$	Possible assignments	10 Dq (cm ⁻¹)	\mathbf{B} (cm^{-1})	β
[CrL ³ Cl ₂]Cl	3.38	35,000 27,000 19,047	1.52	$\begin{array}{l} {}^{4}T_{1g}(P) \longleftarrow {}^{4}A_{2g}(F) \\ {}^{4}T_{1g}(F) \longleftarrow {}^{4}A_{2g}(F) \\ {}^{4}T_{2g}(F) \longleftarrow {}^{4}A_{2g}(F) \end{array}$	12,202	1,020	0.99
[MnL ³ Cl ₂]	3.89	34,000 24,000 21,000	1.68	$\begin{array}{l} {}^{4}\Gamma_{1g}(P) \leftarrow {}^{6}A_{1g} \\ {}^{4}E_{g}(G) \leftarrow {}^{6}A_{1g} \\ {}^{4}T_{1g}(G) \leftarrow {}^{6}A_{1g} \end{array}$	9,002	740	0.77
[FeL ³ Cl ₂]Cl	5.98	36,363 28,751 25,000 19,000	1.71	Charge transfer ${}^{4}E_{1g}(D) \leftarrow {}^{6}A_{1g}$ ${}^{4}A_{1g}(G) \leftarrow {}^{6}A_{1g}$ ${}^{4}T_{1g}(G) \leftarrow {}^{6}A_{1g}$	11,990	980	0.89
[CoL ³ Cl ₂]	4.41	21,505 17,699 14,925	1.66	$\begin{array}{l} {}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}(F) \\ {}^{4}A_{2g}(F) \leftarrow {}^{4}T_{1g}(F) \\ {}^{4}T_{2g}(F) \leftarrow {}^{4}T_{1g}(F) \end{array}$	10,110	820	0.84
[NiL ³ Cl ₂]	3.34	25,000 17,241 13,157	1.62	$\begin{array}{l} {}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F) \\ {}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}(F) \\ {}^{3}T_{2g}(F) \leftarrow {}^{3}A_{2g}(F) \end{array}$	11,210	960	0.88

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Charge transfer ${}^{4}E_{g} \leftarrow {}^{2}B_{1g}$ ${}^{2}A_{1g} \leftarrow {}^{2}B_{1g}$

28,000 15,000 12,981

1.99

[CuL³Cl₂]

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Figure 2. General structure for the M(II) complexes (M(II) = MN(II), Co(II), Ni(II), Cu(II) and Zn(II)).

The Cu(II) complexes with all of the three ligands show a charge transfer and a broad band in the 13,000–16,000 cm⁻¹ region assigned to the ${}^{2}T_{2g} \leftarrow {}^{2}E_{g}$ transition which is characteristic of an octahedral geometry for the Cu(II) ion. The magnetic moment values also support the above geometry for the Cu(II) ion.

In the case of small macrocycles, the field strength of the ligand is affected by the ring size, especially in N_4 ligands.^[17] The ring which fits a given metal ion produces a normal ligand field but when the size of the metal ion is relatively



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smaller it shows an abnormally large ligand field. In order to reduce strain, smaller rings get folded during chelation or the metal ions are kept on top of the ring as in the case of heme.^[18] However, the ionic radii of Co(II), Cu(II) and Zn(II) ions are almost identical (73–75 pm). They may match the cavity provided by the ring,^[18] while the Cr(III), Fe(III) and Ni(II) ions, (61.5–69.0 pm) appear to be loosely fitted. Mn(II) is fairly large (83.0 pm) and it may, therefore, sit on top of the hole of the ring and may undergo appreciable distortion.

EXPERIMENTAL

Synthesis of N,N-Diphenyloxamide and N,N-Dipyridyloxamide

NaOH (20 mmol, 0.80 g) dissolved in the minimum amount of water was added to aniline (20 mmol, 1.86 mL) or 2-aminopyridine (20 mmol, 1.88 g) in ethanol (25 mL). Diethyl oxalate (10 mmol, 1.35 mL) was then added and the mixture was heated to 60 °C for 4 h with continuous stirring. It was then cooled to 0 °C and an excess of 10% HCl was added causing immediate precipitation of a white product which was washed with ethanol and crystallized from a 2:1 mixture of ethanol and an aqueous buffer of pH 4 prepared from a mixture of 8 mL of 0.2 N acetic acid and 2 mL of 0.2 N sodium acetate.^[19]

Synthesis of L^1 , L^2 and L^3

1,3-Diaminopropane (20 mmol, 1.3 mL) was added drop-wise to N,Ndicarboxymethyloxamide (20 mmol, 4.08 g) dissolved in the 100 mL ethanol buffered at pH 4 at ambient temperature and refluxed for about 20 h. This mixture was cooled to -5 °C and an excess of 10% HCl was added and the mixture was then left for two days at this temperature, which afforded a white product. It was recrystallized from a 1:1 mixture of ethanol and aqueous buffer of pH 4. Yield, 1.6 g (30%).

 L^2 and L^3 were synthesized by the same procedure using N,N-diphenyloxamide and N,N-dipyridyloxamide in place of N,N-dicarboxy-methyloxamide. Yields, 1.5 g (24%) and 1.3 g (22%), respectively.

Synthesis of Complexes

A mixture of hydrated metal chloride (1 mmol) in 20 mL methanol and the ligand (1 mmol) dissolved in a mixture of 10 mL ethanol and 10 mL of an





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aqueous buffer of pH 4 was heated on a water bath for 6 h, which yielded a precipitate. It was filtered, washed with ethanol and dried *in vacuo*.

Materials and Methods

Glycine, aniline, 2-aminopyridine, diethyl oxalate, hydrated metal salts (BDH) and 1,3-diaminopropane (Koch Light) were used as received. N,N-dicarboxymethyloxamide was synthesized by the literature method.^[20]

Elemental analyses were carried out with a Thomas and Coleman analyzer. The metals were determined by complexometric titration and chloride was determined gravimetrically.^[21] The IR spectra ($4000-200 \text{ cm}^{-1}$) were recorded on a 621 Perkin–Elmer grating spectrophotometer as KBr disc. The electronic spectra were recorded on a Carl-Zeiss VSU2P spectrometer in DMSO. Magnetic susceptibility measurements were done with a model 155 Allied Research vibrating sample magnetometer and the molar conductances were measured at room temperature using a Systronics 321 conductivity bridge. The NMR spectra were recorded on a Varian A-60 D spectrometer.

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