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Template Synthesis and Characterization of 12 and 14-Membered Pendant-Armed Tetraazamacrocyclic Transition Metal Complexes: A Photoelectron Spectroscopic Study

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## Template Synthesis and Characterization of 12 and 14-Membered Pendant-Armed Tetraazamacrocyclic Transition Metal Complexes: A Photoelectron Spectroscopic Study

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## ABSTRACT

A new series of 12 and 14-membered tetraazamacrocyclic complexes,  $[ML^1X_2]$  and  $[ML^2X_2]$  [M = Mn(II), Zn(II), Co(II), Ni(II), X = Cl];  $[ML^1X_2]$  and  $[ML^2X_2]$  [M = Cu(II), X = Cl or  $NO_3$ ,  $L^1$  and  $L^2 = 12$ and 14-membered tetraazamacrocyclic ligands] have been prepared via the template condensation of 1,2-dibromoethane or 1,3-dibromopropane with aniline. The complexes have been characterized by elemental analyses, conductivity, IR, UV-VIS, <sup>1</sup>H NMR, magnetic susceptibility

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measurements, and x-ray photoelectron spectra. An octahedral geometry has been assigned for all of the prepared metal complexes.

*Key Words:* Magnetic susceptibility measurements; X-ray photoelectron spectra; Metal complexes; Template condensation.

## **INTRODUCTION**

Transition metal complexes of macrocyclic ligands have been studied for many years.<sup>[1]</sup> Recently, interest has drawn by their catalytic properties, which led to industrial applications.<sup>[2,3]</sup> Macrocyclic complexes are significant as they can be used as catalysts in many organic oxidation reactions<sup>[3]</sup> and they have been found to act as possible models for biochemically important proteins and enzymes.<sup>[4-8]</sup> Macrocyclic polyamides of different ring sizes have been reported extensively in the literature.<sup>[9–17]</sup> Macrocyclic compounds containing nitrogen and other heteroatoms as ring components have usually been prepared by use of either the high dilution technique<sup>[13-15,18-20]</sup> or by metal template reactions.<sup>[21-25]</sup> Recently, a new route for the preparation of 14-22 membered tetraamide macrocyclic ligands using dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine as condensing reagents was reported.<sup>[26]</sup> Herein, we report the synthesis and characterization of a new series of 12 and 14-membered pendant-armed tetraazamacrocyclic transition metal complexes (Fig. 1), obtained by the template condensation reaction of 1,2-dibromoethane or 1,3-dibromopropane with aniline.

## **RESULTS AND DISCUSSION**

The complexes may be synthesized by the following general method. Pendant-armed tetraazamacrocyclic transition metal complexes ( $[ML^1X_2]$ ,  $[ML^2X_2]$ ) can be conveniently be prepared in fair to good yields by the interaction of aniline,1,2-dibromoethane and 1,3-dibromopropane with metal salt under anhydrous condition.

$$\begin{aligned} 4\text{ArNH}_{2} + 4\text{BrCH}_{2}\text{CH}_{2}\text{Br} + MX_{2} &\longrightarrow [\text{ML}^{1}X_{2}] \end{aligned} (1) \\ 4\text{ArNH}_{2} + 2\text{BrCH}_{2}\text{CH}_{2}\text{CH}_{2}\text{Br} + 2\text{BrCH}_{2}\text{CH}_{2}\text{Br} + MX_{2} &\longrightarrow [\text{ML}^{2}X_{2}] \end{aligned} (2) \\ M &= \text{Mn(II), Co(II), Ni(II), Cu(II), Zn(II);} \quad X = \text{Cl}; X = \text{NO}_{3} \end{aligned}$$



M = Cu(II), Mn(II), Zn(II), Co(II), Ni(II)X = CI (X = CI, NO<sub>3</sub> in one case M = Cu(II))

*Figure 1.* 12 and 14-Membered pendant-armed tetraazamacrocyclic transition metal complexes.

All the complexes have shown high melting points. Elemental analyses were within  $\pm 0.5\%$  for C, H, N, Cl, and M and the molar conductance values for all the compounds in DMSO lie in the  $12-25 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$  range, which supports<sup>[34]</sup> the contention that the nature of these complexes is non-ionic. (Table 1). However, we could not grow single crystals suitable for x-ray crystallographic studies.

### **Infrared Spectra**

All of the complexes show bands in at  $1150-1210 \text{ cm}^{-1}$  which may be assigned to  $\nu(\text{C}-\text{N})$  modes. The presence of a band in the region

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Compound	;			Ą	nalysis (	%) found	(calcd)		Molar conductivity $\frac{1}{2}$			e
empirical formula (M.W.)	M.p. (°C)	Yield (%)	Colour	С	Н	z	Μ	CI	$(ohm^{1} cm^{2})$ $mol^{-1}$	$\mu_{\rm eff}$ (B.M.)	$\lambda_{ m max} ( m cm^{-1})$	$\varepsilon (dm^{2} m)^{2}$ mol <sup>-1</sup> cm <sup>-1</sup> )
MnL <sup>1</sup> Cl <sub>2</sub> C <sub>32</sub> H <sub>36</sub> Cl <sub>2</sub> MnN <sub>4</sub> (602.4)	260	28	Pink	63.9 (63.81)	5.8 (5.97)	9.1 (9.29)	9.2 (9.11)	11.6 (11.78)	15	5.66	22,500 18,500 32,100	39
MnL <sup>2</sup> Cl <sub>2</sub> C <sub>34</sub> H <sub>40</sub> Cl <sub>2</sub> MnN <sub>4</sub> (630.5)	267	30	Pink	64.4 (64.79)	6.4 (6.34)	8.6 (8.88)	8.6 (8.71)	11.3 (11.26)	18	5.70	22,600 18,300 32,000	40
CoL <sup>1</sup> Cl <sub>2</sub> C <sub>32</sub> H <sub>36</sub> Cl <sub>2</sub> CoN <sub>4</sub> (606.4)	215	52	Royal blue	63.5 (63.39)	5.8 (5.93)	9.1 (9.23)	9.8 (9.72)	11.8 (11.71)	25	4.10	14,350 21,600	37
CoL <sup>2</sup> Cl <sub>2</sub> C <sub>34</sub> H <sub>40</sub> Cl <sub>2</sub> CoN <sub>4</sub> (634.5)	210	50	Royal blue	64.2 (64.37)	6.2 (6.30)	8.6 (8.82)	9.3 (9.29)	11.3 (11.19)	22	4.15	14,600 21,350	39
NiL <sup>1</sup> Cl <sub>2</sub> C <sub>32</sub> H <sub>36</sub> Cl <sub>2</sub> N4Ni (606.2)	235	27	Grey	63.2 (63.40)	5.8 (5.93)	9.2 (9.23)	9.8 (9.70)	11.8 (11.71)	18	3.12	15,000 23,850	42

Table 1.	Melting points.	yields	(%),	colours,	elemental	analyses,	molar	conductances,	magnetic	moments,	and	spectral d	ata of	сці
compounds.														

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NiL <sup>2</sup> Cl <sub>2</sub> C <sub>34</sub> H <sub>40</sub> Cl <sub>2</sub> N <sub>4</sub> Ni (634.2)	235	29	Dark grey	64.2 (64.39)	6.4 (6.30)	8.8 (8.83)	9.1 (9.27)	11.2 (11.19)	18	3.11	15,700 24,000	43
ZnL <sup>1</sup> Cl <sub>2</sub> C <sub>32</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>4</sub> Zn (613.2)	230	44	Off white	62.5 (62.73)	5.9 (5.87)	9.0 (9.14)	10.4 (10.65)	11.6 (11.58)	20	I	I	
ZnL <sup>2</sup> Cl <sub>2</sub> C <sub>34</sub> H <sub>40</sub> Cl <sub>2</sub> N <sub>4</sub> Zn (641.2)	223	41	Off white	63.6 (63.74)	6.3 (6.24)	8.6 (8.74)	10.0 (10.19)	11.1 (11.08)	21	I	I	
CuL <sup>1</sup> Cl <sub>2</sub> C <sub>32</sub> H <sub>36</sub> Cl <sub>2</sub> CuN <sub>4</sub> (611.0)	129	47	Light black	62.8 (62.92)	5.9 (5.89)	9.6 (9.16)	10.2 (10.39)	11.5 (11.62)	17	1.75	19,300 16,100	38
CuL <sup>2</sup> Cl <sub>2</sub> C <sub>34</sub> H <sub>40</sub> Cl <sub>2</sub> CuN <sub>4</sub> (639.1)	135	52	Light black	63.8 (63.92)	6.1 (6.26)	8.8 (8.76)	9.8 (9.93)	11.2 (11.11)	16	1.78	19,400 15,580	4
CuL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> C <sub>32</sub> H <sub>36</sub> CuO <sub>6</sub> N <sub>6</sub> (664.1)	132	60	Dark black	57.4 (57.88)	5.3 (5.42)	8.0 (8.43)	9.4 (9.56)	I	14	1.80	19,600 15,580	39
CuL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> C <sub>34</sub> H <sub>40</sub> CuO <sub>6</sub> N <sub>6</sub> (692.2)	140	66	Dark black	59.0 (59.01)	5.6 (5.78)	8.0 (8.09)	9.0 (9.17)	I	12	1.82	19,300 16,000	46

 $330-380 \text{ cm}^{-1}$  in the spectra of all of the complexes is assignable to  $\nu$ (M–N) vibrations.<sup>[24]</sup> Bands appearing in the region 3000-3100, 650-750, 1580-1600, and  $1460-1500 \text{ cm}^{-1}$  may be assigned as,  $\nu$ (C–H) aromatic,  $\delta$ (C–H) aromatic,  $\nu$ (C=H) aromatic and  $\nu$ (C–H) aliphatic, respectively.<sup>[24]</sup> All of the complexes shown bands in the region  $265-310 \text{ cm}^{-1}$  assignable to  $\nu$ (M–Cl) vibrations. Bands in the regions 1230-1245, 1000-1030, and  $850-875 \text{ cm}^{-1}$  for the nitrate complexes indicate the presence of monodentate coordinated nitrate groups.<sup>[30]</sup>

## **Electronic Spectra and Magnetic Moments**

The electronic spectra of the cobalt(II) complexes show two bands in the 14,200-14,650 and  $21,350-21,700 \text{ cm}^{-1}$  regions, which may be assigned<sup>[31,32]</sup> to the  ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$  and  ${}^{4}A_{1g}(F) \rightarrow {}^{4}T_{2g}(P)$  transitions, respectively, suggesting an octahedral geometry around the cobalt(II) ion, which is further confirmed by the observed magnetic moment (4.05-4.20 B.M.). The macrocyclic complexes derived from Ni(II) ions show two bands in their electronic spectra in the regions 14,900-15,800 and 23,750- $25,000 \text{ cm}^{-1}$  which may be assigned<sup>[31,32]</sup> to the  ${}^{3}A_{2p}(F) \rightarrow {}^{3}T_{1p}(F)$  and  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$  transitions, respectively, suggesting an octahedral geometry around the nickel(II) ions, which is further confirmed by the observed magnetic moment values (3.10-3.13 B.M.). The electronic spectra all Cu(II) complexes show broad band maxima at  $18,200-19,000 \text{ cm}^{-1}$  with a shoulder on the low-energy side at 15,280-16,620 and 19,100-19,750 cm<sup>-1</sup>, which may be assigned to the  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  and  ${}^{2}B_{1g} \rightarrow {}^{1}B_{2g}$  transitions, respectively, corresponding to octahedral geometry around the copper(II) ion.[31] The magnetic moment values (1.72-1.82 B.M.) further confirm the proposed geometry. The electronic spectra of the Mn(II) complexes show three bands in the ranges at 22,500-22,800 and  $32,000-32,300 \text{ cm}^{-1}$  and the magnetic moment values of all Mn(II) metal complexes (5.62-5.82 B.M.) suggest octahedral geometry around the Mn(II) ion.

## <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR spectra of the  $[ML^{1}X_{2}]$  and  $[ML^{2}X_{2}]$  complexes show a multiplet in the region 2.16–2.20 ppm with an intensity ratio of 16:20 corresponding to the middle-CH<sub>2</sub> protons.<sup>[33]</sup> All of these complexes show a multiplet in the region 7.18–7.30 ppm region due to phenyl ring protons.<sup>[30]</sup> In this region, two peaks, a triplet and a multiplet, corresponding to two side CH<sub>2</sub> groups and two middle-CH<sub>2</sub> groups are seen, respectively.

## Photoelectron Spectroscopy

The photoelectron peak binding energy (BE) data of all metal ions  $(M2p_{3/2,1/2})$ , Cl2p and N1s for MCl<sub>2</sub>, [MLCl<sub>2</sub>] [where M = Mn(II), Co(II), Ni(II), Zn(II)] and for MX<sub>2</sub> and [MLX<sub>2</sub>] [where M = Cu(II), X = Cl, NO<sub>3</sub>] are listed in Table 2. It may be seen that the  $M2p_{3/2,1/2}$  photoelectron peak BE values were observed higher (from 1.8 to 2.2 eV) in metal salts than in the metal complexes (Fig. 2), suggesting that the metal ions have higher election density in the metal complexes than the metal salts due to involvement of the metal ions in coordination.<sup>[28]</sup> Further, the N1s photoelectron peaks have shown higher BE values for all of these metal complexes (402.6–402.8 eV) than free nitrogen atoms (~399 eV), which suggest a more effective positive charge on the nitrogen atom in the metal ion.<sup>[28]</sup> Furthermore, in these metal complexes are coordinated to the metal ion.<sup>[28]</sup> Furthermore, in the case of [CuL(NO<sub>3</sub>)<sub>2</sub>] (where L = L<sup>1</sup> and L<sup>2</sup>) complexes, two nitrogen peaks were observed at 402.8 and 408.4 eV in a 2:1 intensity ratio, out of these two

	Meta	al ion		Nitroge	en (N1s)
Complexes	M2p <sub>1/2</sub>	M2p <sub>3/2</sub>	Cl2p	N	NO <sub>3</sub>
MnCl <sub>2</sub>	653.6	640.6	199.2	_	
$[MnL^1Cl_2]$	652.4	638.8	201.2	402.6	
$[MnL^2Cl_2]$	652.4	638.8	201.2	402.6	_
CoCl <sub>2</sub>	794.8	779.8	199.4		_
$[CoL^1Cl_2]$	793.0	778.0	201.4	402.8	_
$[CoL^2Cl_2]$	793.0	778.0	201.4	402.8	_
NiCl <sub>2</sub>		855.6	199.6		_
$[NiL^1Cl_2]$		853.4	201.6	402.6	_
$[NiL^2Cl_2]$		853.4	201.6	402.6	_
ZnCL <sub>2</sub>	—	1,021.8	199.6	_	
$[ZnL^1Cl_2]$		1,020.0	201.4	402.8	_
$[ZnL^2Cl_2]$		1,020.0	201.4	402.8	_
CuCl <sub>2</sub>	—	931.8	199.8	_	
$[CuL^1Cl_2]$	—	929.8	201.6	402.6	
$[CuL^1Cl_2]$		929.8	201.6	402.6	_
Cu(NO <sub>3</sub> )		931.6	199.4		_
$[CuL^1(NO_3)_2]$		929.6	201.4	402.8	408.4
$[CuL^2(NO_3)_2]$	—	929.6	201.4	402.8	408.4

*Table 2.* Binding energies (eV) in  $[MLCl_2]$  [M = Mn(II), Co(II), Ni(II), Zn(II)] and in  $[MLX_2]$  [M = Cu(II), X = Cl, NO<sub>3</sub>].



*Figure 2.* Mn2p<sub>3/2</sub> BEs (eV) in MnCl<sub>2</sub> and [MnLCl<sub>2</sub>] ( $L = L^1$  or  $L^2$ ) complexes.

N1s photoelectron peaks, one N1s photoelectron peak with low intensity (BE = 408.4 eV) should be due to the NO<sub>3</sub> group and may be assigned to be in inner-sphere coordination.<sup>[28-30,34]</sup>

The Cl2p photoelectron spectra of all complexes have shown higher BE values in the range 201.2-201.4 eV than the starting materials MCl<sub>2</sub> (Table 2), which suggest that in all of the metal complexes chloride ion is coordinated in the inner coordination sphere of the metal ion.<sup>[30]</sup>

The M3s photoelectrons of all of these metal complexes have shown multiple splitting,<sup>[30]</sup> suggesting paramagnetic behaviour, as is consistent with the electronic spectral and magnetic moment data during the present study.

#### EXPERIMENTAL

The metal salts  $MnCl2 \cdot 4H_2O$ ,  $NiCl_2 \cdot 6H_2O$ ,  $CoCl_2 \cdot 6H_2O$ ,  $CuCl_2 \cdot 2H_2O$ ,  $Cu(NO_3)_2 \cdot 3H_2O$ ,  $ZnCl_2$  (all BDH) were commercially available pure samples. 1,2-Dibromoethane (Fine Chem.), 1,3-dibromopropane and aniline (BDH) were used after purification.<sup>[37]</sup> Solvents were distilled and dried by conventional methods.<sup>[37]</sup> Elemental analyses were obtained at the Micro-analytical Laboratory of CDRI, Lucknow, India. Conductance measurements were obtained in DMSO at room temperature using a Digisun electronic conductivity bridge. The UV-Vis spectra of the compounds in DMSO were

recorded on a Pye-Unicam 8800 spectrophotometer at room temperature. The IR spectra.  $(4000-200 \text{ cm}^{-1})$  of all prepared complexes were recorded as KBr discs on a Perkin-Elmer 621 spectrophotometer. <sup>1</sup>H NMR spectra, recorded in DMSO-d<sub>6</sub> using a Bruker AC 200 E spectrometer with Me<sub>4</sub>Si as an internal standard, were obtained at the IIT Kanpur, India. Metals and chloride were determined volumetrically<sup>[35]</sup> or gravimetrically,<sup>[36]</sup> respectively. The magnetic susceptibility was measured by the Faraday method using a Cahn magnetic susceptibility system. Hg[Co(CNS)<sub>4</sub>] was used as a standard for calibration.<sup>[27]</sup> The x-ray photoelectron spectra were recorded on a V.G. Scientific ESCA-3MK II electron spectrometer. The MgK<sub> $\alpha$ </sub> x-ray line (1253.6 eV) was used for photo-excitation. The Cu2p<sub>3/2</sub> (BE = 932.8  $\pm$  0.2) and Au4f<sub>7/2</sub>  $(BE = 83.8 \pm 0.1)$  lines were used to calibrate the instrument and Ag3d<sub>5/2</sub> (BE = 368.2) was used for cross checking.<sup>[28]</sup> All spectra were recorded using the same spectrometer parameters of 50 eV pass energy and 4 mm slit width. The reduced full width at half height maximum (FWHM) at the Au4 $f_{7/2}$  (BE = 83.8 eV) level under these conditions was 1.2 eV. The powdered sample was mixed with high-purity silver powder to reduce the charging effect. A thin layer of such a sample was pressed on a gold metal gauze which was welded to a nickel sample holder. The  $Ag3d_{5/2}$  level (Eb 368.2 eV) obtained from this sample was sharp and did not show any observable shift. Thus, the charging of the sample, if at all present, was negligible.<sup>[28]</sup> The spectra were recorded in triplicate in the region of interest. In most cases, the BEs were reproducible within  $+0.1 \,\mathrm{eV}$ . The usual least-squares fitting procedure of determining peak positions, line widths and areas was used.

#### Synthesis of the Complexes

 $[ML^1X_2]$ 

The divalent metal salts (1 mmol) were dissolved in methanol (15 mL) in a round bottom flask and aniline (1.8 mL, 4 mmol) in methanol (10 mL) and 1,2-dibromoethane (1.8 mL, 4 mmol) in methanol (10 mL) were added drop-wise to the round bottom flask and the resulting mixture was refluxed for 3 hr until a precipitate appeared which was filtered and washed with methanol and dried *in vacuo*. It was further purified on an alumina column using a solution in DMSO and ethylacetate (85%), methanol (10%) and acetic acid (5%) as eluent. The purity of the final product was checked by TLC of the complexes in DMSO solution using ethylacetate (85%), methanol (10%), and acetic acid (5%) as eluent. Only one spot was observed in each case after developing in an iodine chamber, indicating that the compounds were pure.

 $[ML^2X_2]$ 

The same procedure was adopted as above but using 1,3-dibromopropane (2 g, 2 mmol) and 1,2-dibromoethane (0.9 mL, 2 mmol) in place of 1,2-dibromoethane. It was further purified on an alumina column using a solution in DMSO and ethylacetate (85%), methanol (10%) and acetic acid (5%) as eluent. The purity of the recrystallized products (in DMSO and pet.-ether 9:1) in both cases was checked by the TLC technique described previously.

On the basis of all of above mentioned results, the proposed structure of  $[MLX_2]$  complexes (where  $L = L^1$  and  $L^2$ , X = Cl or NO<sub>3</sub>) may be assigned as shown in Fig. 1.

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