

# Template synthesis and characterization of 16-membered octaazamacrocyclic complexes: a photoelectron spectroscopic study

Abul KALAM<sup>1</sup>, Vishnu TRIPATHI<sup>1</sup>, Shekhar SRIVASTAVA<sup>1,\*</sup>  
Yogesh PANDEY<sup>2</sup>, Anil KUMAR<sup>2</sup>, Alok GUPTA<sup>2</sup>, Sharat SRIVASTAVA<sup>2</sup>  
Ankoor PUROHIT<sup>2</sup>

<sup>1</sup>University of Allahabad, Allahabad-211002, INDIA

*e-mail: shekhsri@rediffmail.com, kalam\_abul@rediffmail.com, abul\_k33@yahoo.com*

<sup>2</sup>Department of Chemistry, Bipin Bihari (P.G.) College,  
Jhansi-284128, INDIA

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A novel series of complexes of the type  $[MLX_2]$  where  $M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$  and  $\text{Zn(II)}$ ;  $X = \text{C}^-$  or  $\text{NO}_3^-$  were synthesized by template condensation of hydrazine hydrate, acetaldehyde, 2,4-pentanedione, and thiocarbohydrazide in the presence of divalent metal salt in methanolic solution. The complexes were characterized with the help of elemental analysis, conductance measurements, magnetic measurements, electronic, NMR, XPS, and infrared and far infrared spectral studies. Electronic spectra along with magnetic moments suggest 6-coordinated octahedral geometry for these complexes. The low value of molar conductance indicates them to be non-electrolytes.

**Key Words:** Macrocyclic ligands, transition metal, template condensation.

## Introduction

Synthetic macrocyclic complexes of transition metals have attracted much attention as promising objects in coordination and supramolecular chemistry.<sup>1</sup> The chemistry of transition metal macrocycles is extensive because of their close relationship to molecules of biological significance.<sup>2–5</sup> The importance of these complexes is due to the role they play as models for protein metal binding sites in biological systems, as synthetic

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\*Corresponding author

ionophores,<sup>6</sup> electrocatalysts in fuel cells,<sup>7</sup> MRI contrast agents,<sup>8,9</sup> luminescent sensors,<sup>10</sup> anticancer drugs,<sup>11</sup> and radioimmunotherapeutic agents.<sup>12</sup> These extensive applications have been worth investigating for the design of new macrocyclic ligands for biological and industrial applications. Coordination compounds containing macrocyclic ligands have been studied in recent decades owing to their wide applications in biological and sensor fields.<sup>13,14</sup>

Over the past decades great attention has been devoted to the design and synthesis of Schiff bases with enhanced ability to selectively encapsulate the given metal ion.<sup>15,16</sup> A large number of macrocycles<sup>17,18</sup> and their complexes with transition metal ion have been synthesized and characterized. Several macrocyclic ligands derived from hydrazine and thiocarbohydrazine precursors have been reported.<sup>19,20</sup> In the present paper, we report the synthesis and characterization of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) octaazamacrocyclic complexes, [MLX<sub>2</sub>] {M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), and [X = Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup>]} obtained by the template condensation reaction of hydrazine, acetaldehyde, acetyl acetone, and thiocarbohydrazide, as shown in the Scheme.

## Experimental

The metal salts MnX<sub>2</sub>·4H<sub>2</sub>O, CoX<sub>2</sub>·6H<sub>2</sub>O, NiX<sub>2</sub>·6H<sub>2</sub>O, CuX<sub>2</sub>·2H<sub>2</sub>O, and ZnX<sub>2</sub> (X= Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup>) (all BDH) were commercially available pure samples. The chemicals hydrazine monohydrate, 2,4-pentanedione (Fluka), acetaldehyde (BDH), thiocarbohydrazide (Alfa Aesar), and all solvents (AR grade) were purified as described elsewhere prior to use.<sup>21</sup>

**Synthesis of dichloro/nitrato [2, 5, 8, 10, 13, 16-hexamethyl-3, 4, 6, 7, 11, 12, 14, 15-octa azacyclohexadecane-2, 7, 10, 15-tetraene) metal (II), [MLX<sub>2</sub>] (M = Mn(II), Co(II), Ni(II), Cu(II), and Zn(II); X = Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup>)**

To a methanolic solution (25 mL) of hydrazine hydrate (0.002 mmol, 0.198 mL) was added dropwise a methanolic solution (25 mL) of acetaldehyde (99%) (0.001 mmol, 1.13 mL), followed by stirring for 7 h. To this mixture a methanolic solution (25 mL) of the metal salt (0.001 mmol) was added, followed by the addition of 2,4-pentanedione (0.002 mmol, 0.21 mL) and hot solution of thiocarbohydrazide (0.001 mmol). The resulting mixture was refluxed for 9 h until a precipitate appeared, which was filtered, washed 3 times with methanol, and dried over calcium chloride in vacuo. The purity of the final product was checked by TLC on silica gel-G of the complexes in DMSO solution using anhydrous methanol (50%), and tetrahydrofurane (50%) as eluent. Only one spot was observed in each case after developing in an iodine chamber, indicating that the complexes were pure.

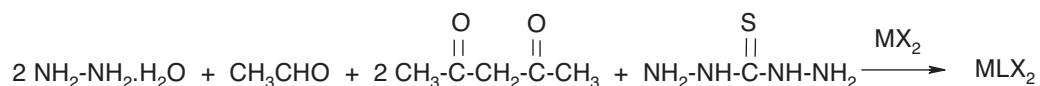
## Characterization of the complexes

Elemental analyses were performed at the microanalytical laboratory of CDRI, Lucknow, India. Metals and chlorides were determined volumetrically<sup>22</sup> and gravimetrically<sup>23</sup> respectively. The IR spectra (4000-200 cm<sup>-1</sup>) of all prepared complexes were recorded as CsI disks on a Perkin-Elmer 621 spectrophotometer. The electrical conductivity of 10<sup>-3</sup> M solution in DMSO was obtained on a Digisum Electronic Conductivity Bridge at room temperature. <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. The UV-Vis spectra of the compounds in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer at room temperature. The magnetic susceptibility was measured by the Faraday method using a Cahn magnetic susceptibility system.  $\text{Hg}[\text{Co}(\text{CNS})_4]$  was used as the standard for calibration.<sup>24</sup> The X-ray photoelectron spectra were recorded on a V.G. Scientific ESCA-3MK II electron spectrometer. The Mg  $K_\alpha$  X-ray line (1253.6 eV) was used for photo-excitation. The Cu  $2p_{3/2}$  (BE =  $932.8 \pm 0.2$ ) and Au  $4f_{7/2}$  (BE =  $83.8 \pm 0.1$ ) lines were used to calibrate the instrument and Ag  $3d_{5/2}$  (BE = 368.2) was used for cross checking.<sup>25</sup> All the spectra were recorded using the same spectrometer parameter of 50 eV pass energy and 4 mm slit width. The reduced full width at half height maximum (FWHM) at the Au  $4f_{7/2}$  (BE = 83.2 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 gold metal gauze, which was welded to a nickel sample holder. The Ag  $3d_{5/2}$  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>25</sup> The spectra were recorded in triplicate in the region of interest. In most cases the binding energies were reproducible within  $\pm 0.1$  eV. The usual least-squares fitting procedure of determining peak positions, line widths, and areas was used.

## Results and discussion

A series of octaazamacrocyclic complexes  $[\text{MLX}_2]$  were synthesized by the template condensation of hydrazine, acetaldehyde, acetyl acetone, and thiocarbohydrazine with metal ions in a 2:1:2:1:1 molar ratio, which may be represented by the following reactions:



where M= Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); X = Cl,  $\text{NO}_3$

All complexes are stable to the atmosphere and had high melting points. Elemental analyses were within  $\pm 0.5\%$  for C, H, and N and the low molar conductance values of all the compounds in DMSO at room temperature, which supports<sup>26</sup> the contention that these complexes are non-ionic (Table 1). However, we could not grow single crystals suitable for X-ray crystallographic studies.

The IR spectrum did not exhibit any band corresponding to the free amino and ketonic groups. A new weak band appeared in the  $1580\text{-}1620 \text{ cm}^{-1}$  region in the IR spectra of all the complexes, which may be assigned to the imine  $\nu$  (C=N) stretching vibration<sup>27</sup>. This is in support of the formation of the azomethine group during the condensation. This range of  $\nu$  (C=N) vibrations is in the region reported for the coordinated C=N<sup>28</sup> group. The medium intensity bands that appeared in the  $410\text{-}445 \text{ cm}^{-1}$  region are assignable<sup>29</sup> to  $\nu$  (M-N) vibrations. The appearance of the sharp single band in the  $3210\text{-}3248 \text{ cm}^{-1}$  region assignable to the condensed N-H group<sup>30</sup> and the absence of bands characteristic of the  $\text{NH}_2$  groups of the hydrazine moiety support the proposed condensation. This is further confirmed by the appearance of a characteristic  $\nu$  (C-N) band at around  $1160\text{-}1200 \text{ cm}^{-1}$ . The coordination of the nitrate and chloro groups was ascertained by bands in the  $235\text{-}255$  and  $255\text{-}310 \text{ cm}^{-1}$  region, which may reasonably be assigned<sup>29-31</sup> to  $\nu$  (M-O) and  $\nu$  (M-Cl).

**Table 1.** Melting points, yields (%), colors, elemental analyses, molar conductance, magnetic moments and spectral data of the compounds.

Compounds Empirical formula (M.W.)	M.p. (°C)	Yield (%)	Color	Analyses (%) found (calc)			Molar conductivity (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	$\mu_{\text{eff}}$ (B.M.)	$\epsilon$ (dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )
				C	H	N			
MnLCl <sub>2</sub> C <sub>13</sub> H <sub>36</sub> Cl <sub>2</sub> MnN <sub>8</sub> S (448.04)	254	52	Pink	34.5 (34.6)	5.2 (5.3)	24.7 (24.8)	19	5.86	38
MnL(NO <sub>3</sub> ) <sub>2</sub> C <sub>13</sub> H <sub>36</sub> MnO <sub>6</sub> N <sub>10</sub> S (515.14)	261	50	Pink	31.1 (31.0)	4.6 (4.7)	2.6 (2.7)	20	5.90	40
CoLCl <sub>2</sub> C <sub>13</sub> H <sub>36</sub> Cl <sub>2</sub> CoN <sub>8</sub> S (453.04)	192	60	Brown	34.2 (34.3)	5.3 (5.2)	24.5 (24.6)	15	4.56	36
CoL(NO <sub>3</sub> ) <sub>2</sub> C <sub>13</sub> H <sub>36</sub> CoO <sub>6</sub> N <sub>10</sub> S (519.14)	186	57	Violet	30.8 (30.7)	4.8 (4.7)	27.7 (27.6)	11	4.62	39
NiLCl <sub>2</sub> C <sub>13</sub> H <sub>36</sub> Cl <sub>2</sub> NiN <sub>8</sub> S (452.79)	238	49	Smoke grey	34.4 (34.3)	5.3 (5.2)	24.5 (24.6)	23	3.10	43
NiL(NO <sub>3</sub> ) <sub>2</sub> C <sub>13</sub> H <sub>36</sub> NiO <sub>6</sub> N <sub>10</sub> S (518.89)	233	55	Sky blue	30.6 (30.7)	4.6 (4.7)	27.5 (27.6)	18	2.99	45
CuLCl <sub>2</sub> C <sub>13</sub> H <sub>36</sub> Cl <sub>2</sub> CuN <sub>8</sub> S (457.65)	175	42	Bottle green	34.1 (34.0)	5.1 (5.2)	24.5 (24.4)	26	1.75	37
CuL(NO <sub>3</sub> ) <sub>2</sub>	191	47	Olive	30.3	4.7	27.4	23	1.73	40

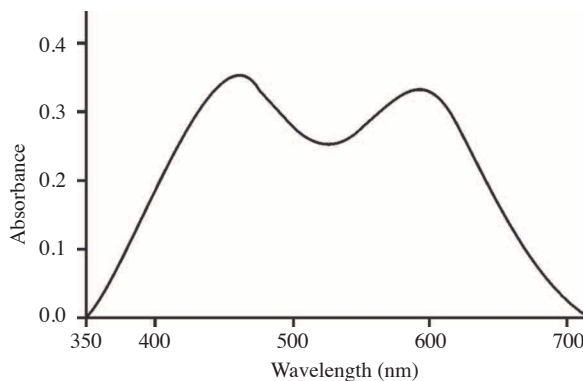
The <sup>1</sup>H-NMR spectrum of octaazamacrocyclic complexes [MLX<sub>2</sub>] does not give any signal corresponding to primary amine protons. It gives a doublet at 8.57 ppm, which is due to the thio-amide group (-NH-CS; 2H) protons.<sup>32</sup>

The <sup>1</sup>H-NMR spectra of the Zn(II) complexes show a sharp signal at 2.45-2.50 ppm corresponding to imine methyl (CH<sub>3</sub>-C=N; 12 H) protons.<sup>33</sup> A singlet observed in the region 2.20-2.30 ppm may be assigned<sup>34,35</sup> to methylene (C-CH<sub>2</sub>-C; 4H) protons of the 2, 3-pentanedione. The spectra show a doublet in the 1.80-1.82 ppm range due to the methyl protons (CH<sub>3</sub>; 3H) of the acetaldehyde moiety. A multiplet in this 1.50-1.53 ppm region may be assigned to (N-CH-N; 1H) of the aldehyde moiety. The <sup>1</sup>H-NMR data for all mononuclear Zn(II) complexes show a broad singlet at 6.28-6.30 ppm due to the protons of the -NH group.<sup>36</sup>

The manganese(II) complexes show a magnetic moment at room temperature in the range of 5.83-5.97 BM corresponding to 5 unpaired electrons. The electronic spectra of the Mn(II) complexes exhibit 3 weak intensity absorption bands in the ranges 18,519-18,911 cm<sup>-1</sup> and 22,553-23,105 cm<sup>-1</sup>, and 37,583-38,129 cm<sup>-1</sup> (Table 1). These bands may be assigned to the transitions: <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub> (<sup>4</sup>G), <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>E<sub>g</sub>, respectively.<sup>37,38</sup>

At room temperature the magnetic moment measurements of cobalt(II) complexes lie in the range 4.89-4.97<sup>39</sup> corresponding to 3 unpaired electrons (Table 1).

The electronic spectra of all the cobalt(II) complexes (Figure 1) exhibit absorptions in the regions 16,900-17,000 and 21,700-21,750  $\text{cm}^{-1}$ . These bands may be assigned to the transitions:  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ , respectively. The position of these bands indicates that these complexes have an octahedral geometry.<sup>40</sup>



**Figure 1.** Electronic spectra of  $[\text{CoL Cl}_2]$  complex.

Nickel(II) with electronic configuration  $d^8$  shows a tendency to form square planar complexes with strong field ligand and octahedral complexes with weak field ligands. At room temperature the magnetic moment measurements of nickel(II) complexes lie in the range 2.99-3.10 BM corresponding to 2 unpaired electrons. The observed magnetic moments<sup>41</sup> for all complexes are consistent with the high spin octahedral geometry around the metal ions, which indicates that the ligand field is weak, and it is probable that nickel(II) assumes an octahedral geometry rather than a square planar geometry.

This is supported by the appearance of 2 main bands in the 11,200-11,400  $\text{cm}^{-1}$  and 17,500-17,900  $\text{cm}^{-1}$  region in the spectra of Ni(II) complexes. These bands may be assigned to the transitions  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ , respectively. The position of these bands indicates that these complexes have an octahedral geometry.<sup>41</sup>

The magnetic moment measurement of the Cu(II) complexes at room temperature lies in the range 1.73-1.75 BM corresponding to one unpaired electron.<sup>40,42</sup> Electronic spectra of copper(II) complexes exhibit bands in the ranges 15,280-16,620  $\text{cm}^{-1}$  and 18,700-19,000  $\text{cm}^{-1}$ , respectively, corresponding to the following transitions [33]:  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$  ( $d_{xy} \rightarrow d_{zy}$ ) and  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  ( $d_{xy} \rightarrow d_{zy}, d_{yz}$ ), respectively, consistent with the presence of an octahedral geometry.

The photoelectron binding energy (BE) data of all metal ions  $\text{M}2\text{p}_{3/2,1/2}$ ;  $\text{Cl}2\text{p}$  and  $\text{N}1\text{s}$  for  $\text{MCl}_2$ ,  $[\text{MCl}_2]$  and  $[\text{ML}(\text{NO}_3)_2]$  (where  $\text{M} = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$  and  $\text{Zn(II)}$ ) are listed in Table 2. It may be seen that the  $\text{M}2\text{p}_{3/2,1/2}$  photoelectron peak BE values were higher in metal salts than in complexes (Figure 2), suggesting that the metal ions have higher electron density in complexes than the metal salts due to involvement of the metal ions in coordination. Further, the  $\text{N}1\text{s}$  photoelectron peak showed 2 BE values for all these metal complexes, 399.4 eV and 402.6-402.8 eV, than the free nitrogen atom ( $\sim 399$  eV), one for nitrogen from the  $-\text{NH}$  group and the other for nitrogen from the  $-\text{C}=\text{N}$  group. The higher  $\text{N}1\text{s}$  binding energy value  $\sim 402.6$ -402.8 eV suggests a more effective positive charge on the nitrogen atom of the  $-\text{C}=\text{N}$  group in the metal complexes.<sup>25</sup> From these  $\text{M}2\text{p}_{3/2}$  and  $\text{N}1\text{s}$  XPS data one can conclude that the nitrogen atom in these metal

complexes is coordinated to the metal ion<sup>25</sup>. Furthermore, in the case of  $[\text{ML}(\text{NO}_3)_2]$  complexes 3 nitrogen peaks were observed in the range of 399.4 eV; 402.6-402.8 eV, and 408.4-408.6 eV in 2:2:1 intensity ratio; out of these 3 N1s photoelectron peaks, 1 N1s photoelectron peak with low intensity (BE= 408.4-408.6 eV) with higher BE should be due to the  $\text{NO}_3$  group and may be assigned to the inner-sphere coordination.<sup>25</sup> The Cl2p photoelectron peak of  $[\text{MLCl}_2]$  complexes showed higher BE (Figure 3) values in the range 201.2-201.4 eV than the starting materials  $\text{MCl}_2$  (Table 2), which suggests that in all the metal complexes the chloride ion is coordinated in the inner coordination sphere of the metal ion.

The S 2p photoelectron BE were the same in all metal complexes  $[\text{MLCl}_2]$  and  $[\text{ML}(\text{NO}_3)_2]$  as in thiocarbohydrazide, suggesting non-involvement of the sulfur atom in coordination.

On the basis of all of the above-mentioned results, the proposed structure of  $[\text{MLX}_2]$  complexes may be assigned as shown in the Scheme.

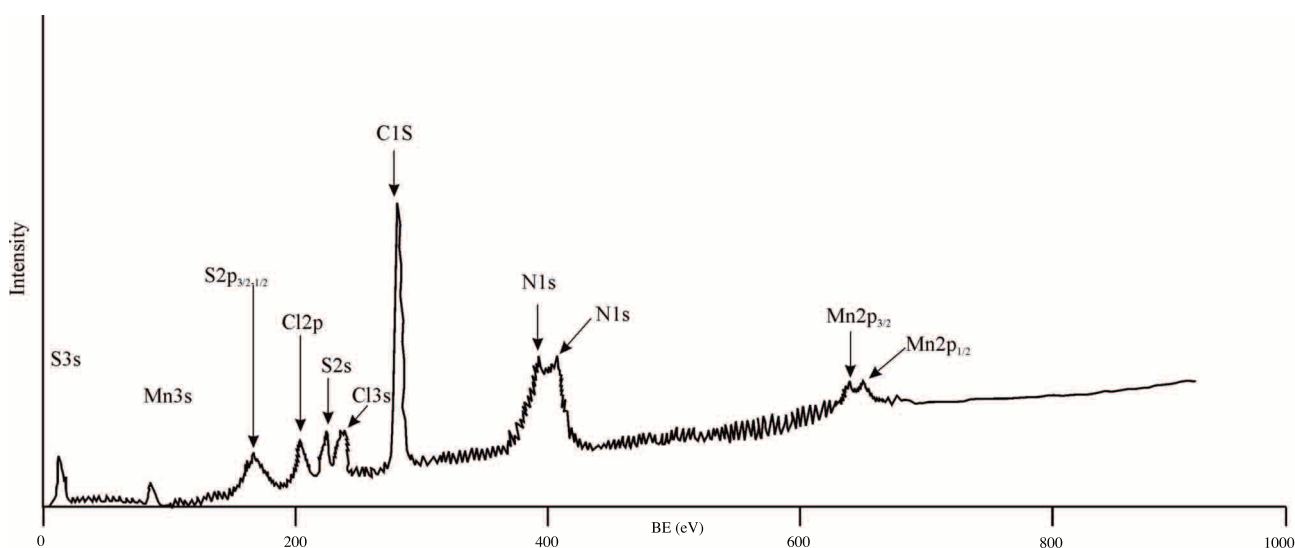


Figure 2. Full scan [0-1000 BE(eV)] XPS spectra of  $\text{MnLCl}_2$  complex.

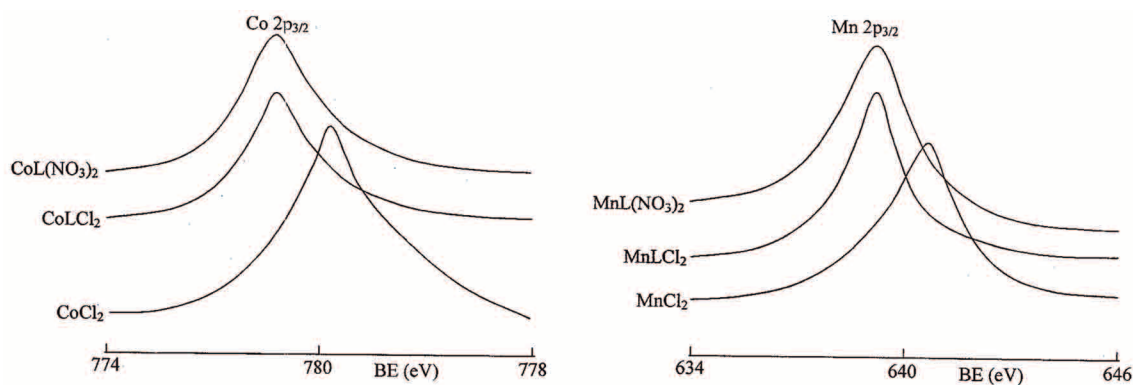
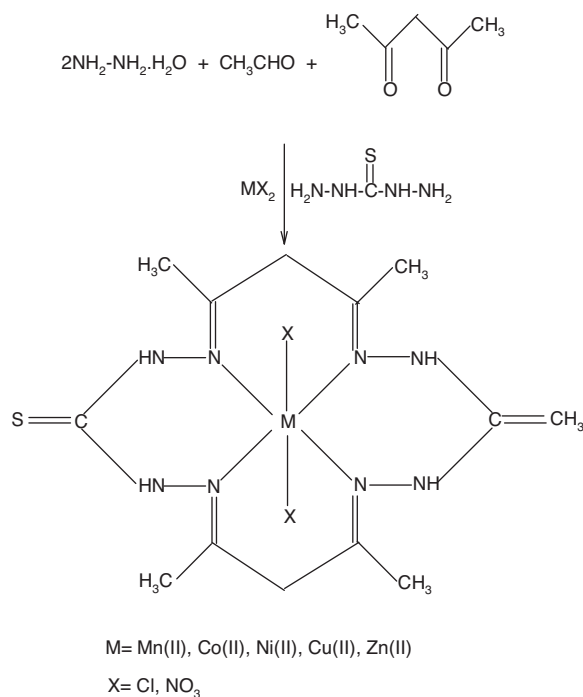


Figure 3. Mn  $2p_{3/2}$  & Co  $2p_{3/2}$  binding energies (eV) in  $\text{MCl}_2$ ,  $\text{MLCl}_2$  and  $\text{ML}(\text{NO}_3)_2$  complexes.

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

Complexes	Metal ion			Nitrogen (N1s)		
	M2p <sub>1/2</sub>	M2p <sub>3/2</sub>	Cl2p	N(from C=N)	N(from NH)	NO <sub>3</sub>
MnCl <sub>2</sub>	653.6	640.6	199.2	–	–	–
MnLCl <sub>2</sub>	652.6	639.0	201.2	402.8	399.4	–
MnL(NO <sub>3</sub> ) <sub>2</sub>	652.8	639.2	–	402.8	399.4	408.6
CoCl <sub>2</sub>	794.8	779.8	199.4	–	–	–
CoLCl <sub>2</sub>	793.6	778.6	201.2	402.6	399.4	–
CoL(NO <sub>3</sub> ) <sub>2</sub>	793.8	778.8	–	402.6	399.4	408.4
NiCl <sub>2</sub>	–	855.6	199.6	–	–	–
NiLCl <sub>2</sub>	–	854.6	201.2	402.6	399.4	–
NiL(NO <sub>3</sub> ) <sub>2</sub>	–	854.8	–	402.8	399.4	408.4
CuCl <sub>2</sub>	–	931.8	199.8	–	–	–
CuLCl <sub>2</sub>	–	930.6	201.4	402.6	399.4	–
CuL(NO <sub>3</sub> ) <sub>2</sub>	–	930.6	–	402.6	399.4	408.4
ZnCl <sub>2</sub>	–	1021.8	199.6	–	–	–
ZnLCl <sub>2</sub>	–	1020.8	201.2	402.6	399.4	–
ZnL(NO <sub>3</sub> ) <sub>2</sub>	–	1020.8	–	402.6	399.4	408.6


**Scheme.** Template synthesis of 16-membered metal complexes.

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