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Synthesis and Characterisation of Chromium (III) Compounds with Tetradentate N_4 Macrocyclic Ligands

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Abstract: *Tetraamidemacrocyclic Ligands (N_4L^1 to N_4L^{44}) have been prepared by the condensation of various primary diamines i.e.- 1, 2- diaminoethane ($NH_2CH_2CH_2NH_2$), 1, 3-diaminopropane ($NH_2CH_2CH_2CH_2NH_2$), 2-methyl-1,3-diaminopropane($NH_2CH_2CH(CH)_3CH_2NH_2$),2,2-dimethyl1,3-diaminopropane ($NH_2CH_2C(CH_3)_2CH_2NH_2$), diethylenetriamine ($NH_2(CH_2)_2NH(CH_2)_2NH_2$)1,6 diaminohexanei.e.$NH_2(CH_2)_6NH_2$,1,7-diaminoheptane$NH_2(CH_2)_7NH_2$,1,8-diaminooctane. $H_2(CH_2)_8NH_2$, 1,9-diaminononane $NH_2(CH_2)_9NH_2$, 1,10-diaminodecane $NH_2(CH_2)_{10}NH_2$ and 1, 12-diaminododecane $NH_2(CH_2)_{12}NH_2$with various dicarboxylic acids i.e. malonic ($(COOH)CH_2(COOH)$), succinic acid ($(COOH)CH_2CH_2(COOH)$), glutaric-($(COOH)CH_2CH_2CH_2(COOH)$), and adipic ($(COOH)CH_2CH_2CH_2CH_2(COOH)$). in the presence of condensing reagents dicyclohexylcarbodiimide and 4- dimethyl aminopyridine, which on reduction give a new series of tetrazamacrocycles ($MacL^1$ to $MacL^{44}$) which forms complexes with $CrCl_3.XH_2O$ These all complexes were characterized by various physicochemical techniques e.g. elemental analysis, molar conductance, UV- visible, IR, ^1H NMR, magnetic moment and XPS data and an octahedral geometry were established for these prepared $[Cr(MacL)Cl_2]Cl$ complexes.*

Keywords: Chromium (III), Macrocyclic ligands, XPS, ^1H NMR.

Introduction

The field of the macrocyclic chemistry of metals is developing very rapidly because of its applications and importance of macrocyclic metal complexes in coordination chemistry and bioinorganic chemistry [1,2,3,]. Many universal macrocyclic ligands such as crown ethers , porphyrins, saturated and unsaturated polyamines, polyazamacrocycles, N_4S_2 donor macrocyclic, Robson type tetraiminodiphenol macrocyclic ligands have been reported in last few decades [4-9]. The studies on complexes of Schiff base macrocyclic ligands with different size, number and donor atoms for coordination with a variety of metal centres have been studied. The template condensation reaction lies in the heart of macrocyclic chemistry. Many transition metal ions in living systems work as enzymes or carriers in macrocyclic ligand environment and used as modelling the active sites of metalloenzymes [10-13]. Macrocyclic metal complexes have been used as metal ion separation, as detecting tumor lesions, as in labeling monoclonal antibodies with radioactive models, as cancer diagnosis, as therapeutic and radio therapeutic, as catalyst, as pharmological agent, as in biological process such as photosynthesis and dioxygen transport, as photosensitizer, as versatile coordination behavior, as toxicity against bacterial fungal growth, as anticancerous, as antitumor, as environmental importance, as potential medicinal applications such as contrast enhancing agents in magnetic resonance imaging (MRI), as NMR shift and relaxation agents as RNA cleavage catalyst[14-25]. The design of host molecules are receptors for the recognition of substrate anion guest molecules in aqueous solution is very important target from an environment, industrial and health related point of view with multiple potential applications[21, 26-28]. The different types of macrocyclic ligands and their metal complexes discoveries have created supramolecular chemistry and its enormous diversity. Very recently few comprehensive reviews on macrocyclic ligands and their metal compound with their applications have been also appeared. Although many Cr(III) macrocyclic complexes have been sythesised and characterized by several physicochemical techniques[29-31] but tetraazamacrocyclic complexes of Cr(III) in which tetraazamacrocyclic ligands (MacL) are formed by preparation of tetraamidemacrocyclic ligands first (N_4L) by condensation of various primary diamines and various decarboxylic acids in the presence of condensing agents dicyclohexylcarbodiimide and 4-dimethyl aminopyridine, then on reduction of these tetramidemacrocyclic ligands, are scare. This paper deals with sysnthesis and characterisation of such type of Cr(III) macrocyclic complexes.

Material and Methods

The entire chemicals were analytical grade and used after purification and drying by conventional methods. The chemicals dicyclohexylcarbodiimide, 4-dimelhylaminopyridine,1,2- diaminoethane,1,3-diaminopropane, 1,2-diaminopropane, 1,6-diaminohexane, 1,7-diaminoheptane, 1,9-diaminononane, 1,10- decane, 1,12 dodecane, $CrCl_3.XH_2O$ or $Cr(NO_3)3XH_2O$ were purchased from the Merck (Mumbai). The organic solvents were used as reagent grade.

Synthesis of the Ligands (N_4L^1-N_4L^{44})

The reaction in carried out in 2:2 molar ratio. The appropriate amount of dicyclohexylcarbodiimide (1.5624g) and catalytic amount of 4-dimethylaminopyridine in minimum amount of dichloromethane at ^{0}C, put on in magnetically stirred two-nacked round bottom flash. The reaction is followed by the addition of 1,2-diaminoethane or 1,3-diaminopropane or 1,2-diaminopropane or 2,2′-dimethyl or 1,6-diaminohexane or 1, 7-diaminoheptane,1, 8-diaminoheptane or 1, 9-diaminononane or 1,10-diaminodecane or 1, 12-diaminododecane (2mmol) in dichloromethane and succinic acid or glotanic acid or malonic acid or adipic acid (2mmol) in dichloromethane. The resulting mixture was stirred for 10-12 hours at ^{0}C.The solid product was isolated by filtration and washed several times with the solvent and dried in vacuo. The solid products were recrystalized from benzene and dried in vacuum.

Synthesis of MacL^1-MacL^{44}

The reaction is carried out in 1:2 molar ratio. The ligands N_4L^1-N_4L^{44} (1.0g) were dissolved in tetrahydrofuran and cooled at 0^0C. Lithium aluminium hydride (corresponding to ligands) in tetrahydrofuran was stirred for about 10 hours in an ice bath. The reaction is followed by mixing the solution of ligand and $LiAlH_4$. The reaction mixture was stirred under reflux for 72 hour. After cooling, 20 ml of 15% aq. NaOH and then 30 ml water were added to the mixture at 0^0C. The solid product was isolated by filtration and the residue repeadly washed with hot tetrahydrofuran. The filtrate was concentrated under reduced pressure. The liquid thus dried in vacuum.

Synthesis of the Complexes

The reaction is carried out in 1: 1 (M: L) molar ratio. 0.9-0.8 g ligands MacL^1-MacL^{44} were dissolved in methanol. The reaction is followed by the addition of $CrCl_3.xH_2O$ or $Cr(NO_3)_3.x\ H_2O$ (corresponding to ligands MacL^1-MacL^{44}) solution. The resulting mixture was stirred for 12 hours at ^{0}C, the solid product was obtained by filtration and washed repeatedly with same solvent and dried in vacuo. The products were recrystalized from benzene.

Physicals measurements

The elemental analysis of C, H and N-were determined on a semi micro scale at CDRI, Lucknow. The molar conductance of the complexes and measured at room temperature at DMF by Digisun Electronics conductivity bridge. The infrared spectra of the complexes and ligands were recorded on perkin-Elmer 457 spectrometer at room temperature in KBr or CsI (for complexes). UU-Visible spectra were obtained on a Perkin Elmer Lambda 900 spectraphotometer. NMR spectra were taken on a Bruker WM 300 MHz spectrometer and on a JEOL FX-200 Teqmac. Magnetic susceptibility was measured by the Faraday method using a Cahn magnetic susceptibility system. Hg $[Co(CNS)_4]$ was used as a standard for calibration[31]. The X-ray photoelectron spectra i.e. XPS were recorded on VG Scientific ESCA-MKII Electron spectrometer. The MgKα X-ray line (1253.6ev) was used for photoexicitation. The Cu2$p_{3/2}$ (BE = 932.8 ±2) and Au47$_{7/2}$ (BE = 83.8 ± 0.1) lines were used to calibrated the instrument and Ag3$d_{5/2}$ (BE = 368.2) was used for crosschecking. All the spectra were recorded using same parameters of 50 eV pass energy and 4 mm slit width. The reduced full width half maximum (FWHM) at Au4$F_{7/2}$ (BE = 83.8 ev) under these condition was 1.2 eV.

The powdered sample mixed with high purity silver powder to reduce the charging effect. A thin layer of such a sample was pressed on a gold metal gauge, which was welded to a nickel sample holder. The Ag 3$d_{5/2}$ level (BE = 368.2eV) obtained from this sample was sharp and did not show any observable shift. Thus, the charging of simple if at all present was negligible[32]. The spectra were recorded in triplicate in the region of interest. Thus, a series of 14-18 membered tetraazamacrocyclic ligands and their complexes was derived by the condensation of dicarboxylic acids with primary diamines in the presence of condensing reagents dicyclohexylcarbodiimide (i.e. DCC) and 4-dimethyl-aminopyridine (i.e. DMP). (Figure1 & 2).

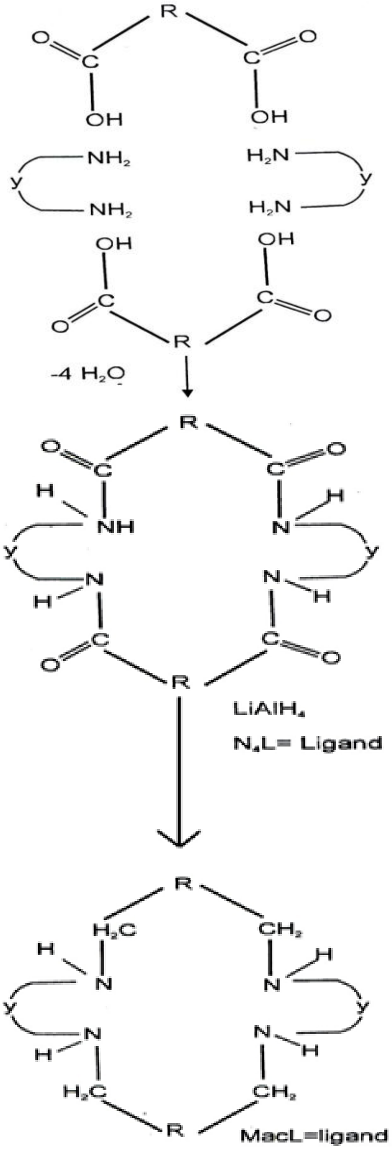
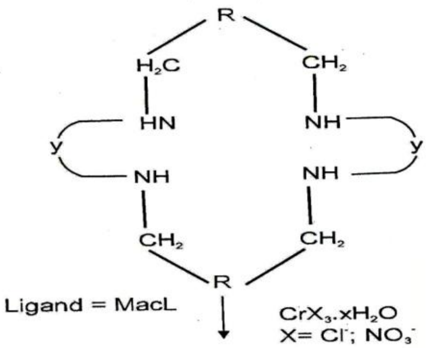


Figure 1: 14-18 membered tetraazamacrocyclic ligands (i.e. MacL^1 to MacL^{44})



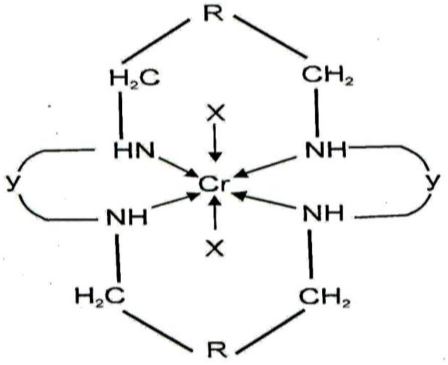


Figure 2: [Cr(MacL)X$_2$] X complexes (Where L = (MacL^1 to MacL^{44})

Results and Discussion

The elemental analysis for C, H, N (found ± 0.5%) and molar conductance data (in DMF 100-120 ohm^{-1} cm^2 mol^{-1}) of these prepared complexes indicated that all these are 1 : 1 electrolyte 120 and may be formulated as [CrLX$_2$] X (Where X = Cl)[33]. The electronic spectra of these Cr(III) complexes in DMSO have shown three bands in the range 15588-16840 cm^{-1} (V$_1$), 18598 – 20135 cm^{-1}(V$_2$) and 21458 – 24858 cm^{-1} (V$_3$). These spin allowed bands, which are shown by six coordinated complexes Oh symmetry and these bands may be assigned to the following transitions: $^4A_{2g}$ (F) $\rightarrow {}^4T_{2g}$(F) $V_1 = E = 10$ Dq, $^4A_{2g}$(F)$\rightarrow {}^4T_{1g}$(F) $V_2 = E = 18$ Dq and $^4A_{2g}$(F)$\rightarrow {}^4T_{1g}$(P)$V_3 = E = 12$ Dq + 15B.

The IR spectra of these prepared Cr (III) metal complexes have shown absence of NH$_2$ stretching vibrations of the amine and – OH groups of the dicarboxylic acids concluding their involvement in the formation of tetraamidemacrocycles. A single sharp band observed for amide ligands NL^1 to NL^{44} in the region 3275 – 3286 cm^{-1} may be assigned toυ (N – H) of amide group. The amide (I), amide (II), amide (III) and amide (IV) groups were shown 1650 – 1710, 1540 – 1580, 1250 – 1278 and 363 – 384 cm^{-1}respectively [34,35] which gives a strong evidence for the presence of a closed cyclic product. The strong and sharp absorption bands were also shown in the region 2820 – 3060 and 1415 – 1480 cm^{-1} in all the complexes were assigned to the C – H stretching and C – H bending vibrational modes respectively[36] . It has been also observed that tetrazamacrocyclesMacL^{1}to MacL^{44} do not show amide bands corresponding to tetraamidemacrocycles. A slight negative shift in the NH stretching vibration has been observed. In the spectra of macrocycle complexes [Cr(MacL^1)Cl$_2$]Cl to [Cr(MacL^{44}) Cl$_2$] Cl as compared to their tetrazamacrocycles ligands, the slight negative shift in the υ (N – H) band that appeared in the region 3218–3230 cm^{-1} was observed. It is assigned to the coordinated N – H stretching vibration, which further proved by the fact that all the complexes have shown a medium intensity band in the region 440 – 460 cm^{-1} which is attributed to Cr ←N stretching vibrations. In all these prepared Cr(III) macrocyclic complexes a band corresponding to υ (M – X) in the region of 330 – 340 cm^{-1} is also present indicating that chlorine is coordinated to Cr(III) metal ion.

Table1: Tetraazamacrocyclic Ligands i.e. $MacL^1$nto $MacL^{44}$

Complexes	y	R
$N_4L^1 = MacL^1 =$	$- CH_2CH_2-$,	$- CH_2-$
$N_4L^2 = MacL^2 =$	$- CH_2CH_2CH_2-$,	$- CH_2-$
$N_4L^3 = MacL^3 =$	$- CH_2CH(CH_3)CH_2-$,	$- CH_2-$
$N_4L^4 = MacL^4 =$	$- CH_2C(CH_3)_2CH2-$,	$- CH_2-$
$N_4L^5 = MacL^5 =$	$- (CH_2)_2NH\ (CH_2)_2-$,	$- CH_2-$
$N_4L^6 = MacL^6 =$	$- (CH_2)_6-$,	$- CH_2-$
$N_4L^7 = MacL^7 =$	$- (CH_2)_7-$,	$- CH_2-$
$N_4L^8 = MacL^8 =$	$- (CH_2)_8-$,	$- CH_2-$
$N_4L^9 = MacL^9 =$	$- (CH_2)_9-$,	$- CH_2-$
$N_4L^{10} = MacL^{10} =$	$- (CH_2)_{10}-$,	$- CH_2-$
$N_4L^{11} = MacL^{11} =$	$- (CH_2)_{12}-$,	$- CH_2-$
$N_4L^{12} = MacL^{12} =$	$- CH_2CH(CH_3)CH_2-$,	$- (CH_2)_2-$
$N_4L^{13} = MacL^{13} =$	$- CH_2CH_2CH_2-$,	$- (CH_2)_2-$
$N_4L^{14} = MacL^{14} =$	$- CH_2CH(CH_3)CH_2-$,	$- (CH_2)_2-$
$N_4L^{15} = MacL^{15} =$	$- CH_2CH(CH_3)CH_2-$,	$- (CH_2)_2-$
$N_4L^{16} = MacL^{16} =$	$- (CH_2)_2NH\ (CH_2)_2-$,	$- (CH_2)_2-$
$N_4L^{17} = MacL^{17} =$	$- (CH_2)_6-$,	$- (CH_2)_2-$
$N_4L^{18} = MacL^{18} =$	$- (CH_2)_7-$,	$- (CH_2)_2-$
$N_4L^{19} = MacL^{19} =$	$- (CH_2)_8-$,	$- (CH_2)_2-$
$N_4L^{20} = MacL^{20} =$	$- (CH_2)_9-$,	$- (CH_2)_2-$
$N_4L^{21} = MacL^{21} =$	$- (CH_2)_{10}-$,	$- (CH_2)_2-$
$N_4L^{22} = MacL^{22} =$	$- (CH_2)_{12}-$,	$- (CH_2)_2-$
$N_4L^{23} = MacL^{23} =$	$- CH_2CH_2-$,	$- (CH_2)_3-$
$N_4L^{24} = MacL^{24} =$	$- CH_2CH_2CH_2-$,	$- (CH_2)_3-$
$N_4L^{25} = MacL^{25} =$	$- CH_2CH(CH_3)CH_2-$,	$- (CH_2)_3-$
$N_4L^{26} = MacL^{26} =$	$- CH_2C(CH_3)_2CH2-$,	$- (CH_2)_3-$
$N_4L^{27} = MacL^{27} =$	$- (CH_2)_2NH\ (CH_2)_2-$,	$- (CH_2)_3-$
$N_4L^{28} = MacL^{28} =$	$- (CH_2)_6-$,	$- (CH_2)_3-$
$N_4L^{29} = MacL^{29} =$	$- (CH_2)_7-$,	$- (CH_2)_3-$
$N_4L^{30} = MacL^{30} =$	$- (CH_2)_8-$,	$- (CH_2)_3-$
$N_4L^{31} = MacL^{31} =$	$- (CH_2)_9-$,	$- (CH_2)_3-$
$N_4L^{32} = MacL^{32} =$	$- (CH_2)_{10}-$,	$- (CH_2)_3-$
$N_4L^{33} = MacL^{33} =$	$- (CH_2)_{12}-$,	$- (CH_2)_3-$
$N_4L^{34} = MacL^{34} =$	$- CH_2CH_2-$,	$- (CH_2)_4-$
$N_4L^{35} = MacL^{35} =$	$- CH_2CH_2CH_2-$,	$- (CH_2)_4-$
$N_4L^{36} = MacL^{36} =$	$- CH_2CH(CH_3)CH_2-$,	$- (CH_2)_4-$
$N_4L^{37} = MacL^{37} =$	$- CH_2C\ (CH_3)\ CH_2-$,	$- (CH_2)_4-$
$N_4L^{38} = MacL^{38} =$	$- (CH_2)_2NH\ (CH_2)_2-$,	$- (CH_2)_4-$
$N_4L^{39} = MacL^{39} =$	$- (CH_2)_6-$,	$- (CH_2)_4-$
$N_4L^{40} = MacL^{40} =$	$- (CH_2)_7-$,	$- (CH_2)_4-$
$N_4L^{41} = MacL^{41} =$	$- (CH_2)_8-$,	$- (CH_2)_4-$

N_4L^{42} = $MacL^{42}$ =	– $(CH_2)_9$–,	– $(CH_2)_4$–
N_4L^{43} = $MacL^{43}$ =	– $(CH_2)_{10}$–,	– $(CH_2)_4$–
N_4L^{44} = $MacL^{44}$ =	– $(CH_2)_{12}$–,	– $(CH_2)_4$–
Where Y and R are in ligand		

The ^{1}HNMR spectra of all these complexes have shown no band for hydroxyl or amino groups suggesting that the proposed macrocyclic complexes have forms after the condensation. A broad signal is observed in the region δ7.80 – 8.26 ppm for amide protons [35,36] in these macrocyclic ligands N_4L^1 to N_4L^{44}. A multiple appearing in the region δ3.35 – δ3.77 ppm could be assinged to the methylene protons (CO–N–CH_2) adjacent to the nitrogen atom. The spectra of N_4L^1 to N_4L^{44} have shown multiplets in the region δ2.08 – δ2.10 ppm assigned to methylene protons of primary diaminesmoeity. A singlet appearing in the region 82.88 – 2.98 and δ3.29 – δ.30 ppm may be assigned to the methylene protons of the dicaroboxylic acid moeity which are adjacent to the nitrogen atoms. The ^{1}H NMR spectra of $MacL^1$ to $MacL^{44}$ do not show any signal assignable to amide protons which suggested the reduction of carboxylic groups. The spectra of tetraazamacrocycles have shown multiplet in the region δ6.28 – 6.41 ppm due to (C–H) secondary amino protons. Another multiplet observed in the region δ2.65 – δ2.73 ppm is attributed to the methylene protons (N–CH_2–C) of acid moiety[37,38]. The magnetic moment of all the prepared Cr(III) macrocycle complexes were recorded at room temperature which were lies in the range of 3.74 to 3.82 BM.

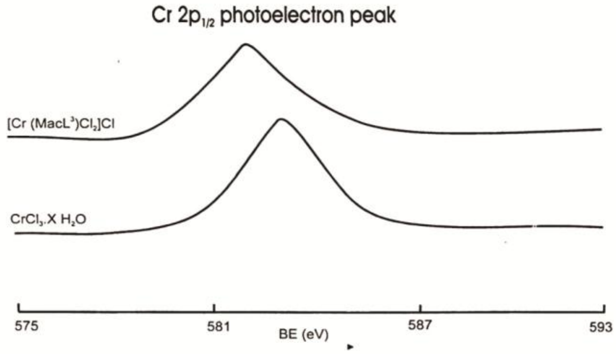


Figure 3: Cr $2p_{1/2}$ BE (eV) in $CrCl_3.XH_2O$ and $[Cr(MacL)Cl_2]$ Cl [L = $MacL^1$, $MacL^2$ and $MacL^3$]

The Cr2P$_{1/3}$’ $_{3/2}$’, N1s and Cl2p binding energies (eV) data of $CrCl_3xH_2O$ and [CrL X_2] X (where X = Cl, L = L_1, L^2..........L^{44}) are recorded and shown in Figure 3, 4 & 5. It may be seen that Cr $2p_{1/2,\ 3/2}$ photoelectron peaks binding energy values were observed in the range of BE~$2p_{1/2}$ 584.6–584.8eV, $2p_{3/2}$ 575.6-575.8eV in [$CrCl_3$ X H_2O] which is more than in metal complexes $[CrLX_2]X$ BE $2p_{1/2}$ 585.6eV and $2p_{3/2}$ 576.6eV (Figure 3).

It suggested that chromium ions have more electron density in metal complexes $[CrLX_2]Cl$ than $[CrCl_3{\cdot}XH_2O]$ due to involvement of metal ion in coordination. Furthermore, N1s photoelectron peak have shown only one symmetrical peak with high binding energy side in metal complexes in the range of BE-402.6 – 402.8 eV $[CrLCl_2]Cl$ than corresponding free ligand N1s binding energy BE at 400.6 eV which suggested all four mitrogen atoms of each ligand is coordinated with Cr(III) metal ion[30] (Figure 4).

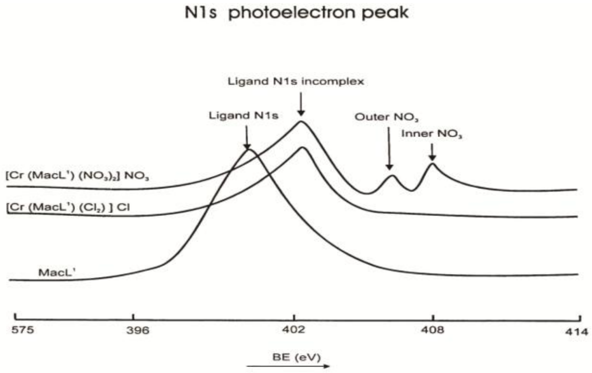


Figure 4: N1s BE (eV) in Ligand $MacL^1$ and [Cr $(MacL)Cl_2$ complexes (where L = $MacL^1$)]

The Cl 2p spectra of all these prepared complexes have shown two peaks with higher BE side than in $CrCl_3{\cdot}XH_2O$ in 1:2 intensity ratio out of these 2p photo electron peaks, one which is towards higher BE side is due to inner chlorine atom and another towards lower BE is due to outer chlorine atom. (Figure 5).

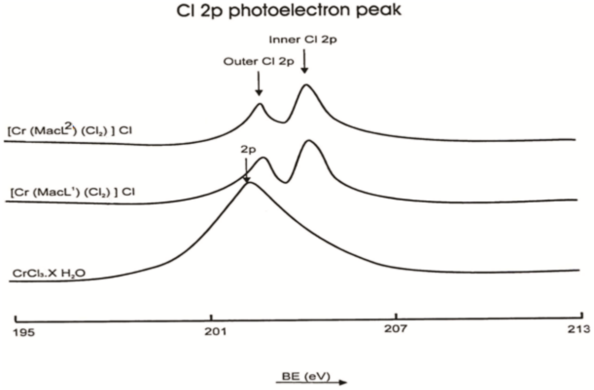


Figure 5: Cl 2p BE (eV) in $CrCl_3$.xH2O, [Cr $(MacL^1)Cl_2$]Cl and [$Cr(MacL^2)Cl_2$]

On the basis of elemental analysis, molar conductance, UV – Visible, IR, NMR, magnetic moment and X-ray photoelectron data, the structure of $[Cr(MacL)Cl_2]Cl$

may be proposed as shown in Figure and an octahedral geometry may be established for them.

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References

1. Siddiqui K.S., Nishat N., Ruthenium(II) Complexes with 8-(Diphenylphosphino) quinoline: Synthesis, Spectroscopic Properties and Single Crystal X-ray Structures Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Organic Chemistry. **29(2)**: 297 **(1999)**

2. Nishat N., Haq M., **Siddiqi K. S., S**ynthesis of quinolinyl hydrazino benzylidene azobenzenes as anti tubercular / anti bacterial agents, *Oriental* Journal of *Chemistry*, **17(1)**: 63 **(2001)**

3. Chandra S., Gupta L.K., Spectroscopic approach in characterization of chromium(III), manganese(II), iron(III) and copper(II) complexes with a nitrogen donor tetradentate, 14-membered azamacrocyclic ligand, *Spectrochimica Acta*, **61**, 2139 **(2005)**

4. Gokel g.w., leevy w. M, Weber M.E., Crown ethers: Sensors for ions and molecular scaffolds for materials and biological models. *Chemical Review*, **104 (5)**: 2723 **(2004)**

5. Hambright P., The coordination chemistry of metalloporphyrins Coord. Chemical. Review, **6**, 247 **(1971)**

6. Kimura E., Macrocyclic polyamines with intelligent functions. *Tetrahedron*. **48**: 6175 **(1992)**

7. Lee K.J., Suh J., Cooperation of Macrocyclic Metal Centers with 4 Dialkylaminopyridines in Catalysis by Poly(ethylenimine)-Based Artificial Metalloesterases. *Bioorganic Chemistry*, **22**: 95 **(1994)**

8. Izatt R.M., Bradshaw J.S., Steven N., John D. Lamb A. et al., Thermodynamic and kinetic data for cation-macrocycle interaction. *Chemical, Review*, **85**: 271 **(1985)**

9. Nelson S.M., Developments in the synthesis and coordination chemistry of macrocyclic Schiff base ligands. *Pure Applied Chemistry*, **52** : 2461 **(1992)**

10. Bértolo E., Bastida R., Blas A.D., Fenton D.E., Lodeiro C., Alejandro M.A., Rodríguez A., Rodríguez-BLAS T., Lanthanide(III) Nitrate Complexes of Two 17 Membered N3O2-Donor Macrocycles. *J. Incl. Phenomena*, **35**: 191 **(1999)**

11. Masoud S.N., Shirin S. A., Mohammad R.G., Parviz N., Synthesis, characterization and catalytic oxidation of cyclohexene with molecular oxygen over host (zeolite-Y)/guest (nickel(II) complexes of R_2[12]1,3-diene$N_2O_2$and R_2[13]1,4-dieneN_2O_2; R = H, Me, Ph) nanocatalyst (HGN). *Transition Metal Chemistry*, **31(7)**: 964 **(2006)**

12. Curtis N.F., Macrocyclic coordination compounds formed by condensation of metal-amine complexes with aliphatic carbonyl compounds. *Coordin. Chem. Rev*., **3**:347**(1968)**

13. Bansal A., Kumar S., Singh R.V., Synthesis and spectroscopic characterization of bivalent lead macrocyclic complexes. **31(6): (2001)**

14. Champness N.R., C.S. Frampton, G. Geid, D.A. Toucher, Mixed phosphathia macrocyclic chemistry: synthesis and characterisation of $[M(Ph_2[14]ane\ P_2S_2)]^{2+}$(M = Pd or Pt) and $[RhCl_2(Ph_2[14]ane\ P_2S_2)]^{+}$($Ph_2$[14]ane P_2S_2= 8, 12-diphenyl-1, 5-dithia-8, 12-diphosphacyclotetradecane). *J. Chem. soc. Dalton Trans.*, **3031 (1994)**

15. Dolphin D., Syntex Award Lecture Photomedicine and photodynamic therapy, *Canadian Journal of Chemistry*, **72**: 1005 **(1994)**

16. Bonnett R., Photosensitizers of the porphyrin and phthalocyanine series for photodynamic therapy. *Chemical Science. Review*, **24**: 19 **(1995)**

17. Maldonado C.R., Salassa L., Gomez-Blanco N., Mareque-Rivas J.C. Nano-functionalization of metal complexes for molecular imaging and anticancer therapy. *Coordination Chemical Review*, **257**: 2668 **(2013)**

18. Pilip M., Bilewicz A., Macrocyclic complexes of scandium radionuclides as precursors for diagnostic and therapeutic radiopharmaceuticals. *J. Inorg. Biochemistry*, **105**: 313 **(2011)**

19. El-Boraey H.A., El-Din A.A.S., Transition metal complexes of a new 15-membered [N_5] penta-azamacrocyclic ligand with their spectral and

anticancer studies, *Spectrochim Acta* A, **132**: 663 **(2014)**

20. Bousquet J.L. and Saini S., Stark D.D., Hahn P.F., Nigam M., Wittenberg J., Ferrucci J.T. Jr.. GD-DOTA: characterization of new paragmatic complexes, *J. Radiology*, **166**: 693 **(1988)**

21. Kong D., Meng L., Song L., Xie Y., Synthesis, structure and antitumor activities of a new macrocyclic ligand with four neutral pendent groups:1,4,7,10-tetrakisbenzyl-1,4,7,10-tetraazacyclododecane (L) and its Co, Ni and Cu complexes. *Transition Metal Chemistry*, **24(5):** 553 **(1999)**

22. Buster D.C., Castro M.M.C.A., Geraldes C.F.G. C., Malloy C.R.A., Sherry D. Siemers T.C., Tm (DOTP)5: A $23Na^+$ shift agent for perfused rat hearts. *Magnetic Resonance in Medicine*, **15**: 25 **(1990)**

23. Bértolo E., Bastida R., Blas A.D., Fenton D.E., Lodeiro C., Alejandro M.A., Rodríguez A., Rodríguez-BLAS T., Lanthanide(III) Nitrate Complexes of Two 17 Membered N_3O_2-Donor Macrocycles, *J. Incl. Phenomena,* **35**: 191 **(1999)**

24. Amin S., Morrow J.R., Lake C.H., Churchill M.R., Lanthanide(III) Tetraamide Macrocyclic Complexes as Synthetic Ribnucleases: Structure and Catalytic Properties of $[La(tcmc)(CF_3SO_3)(EtOH)]$ $(CF_3SO_3)_2$, Angewandte Chemie Int. Edition., **33(7)**: 773 **(1994)**

25. Baker B.F., Khalili H., Wei N., Morrow J.R., Cleavage of the 5‘ Cap Structure of mRNA by a Europium(III) Macrocyclic Complex with Pendant Alcohol Groups. *Journal of American Chemical Society*, **119(38):** 8749**(1997)**

26. Antonisse M.M.G., Reinhoudt D.N., Neutral anion receptors: design and application, *Chem. Commun.*, 44 **(1998)**

27. Steed J.M. and Atwood J.L., Supramolecular chemistry.” Wiley, Chichester, **(2000)**

28. Timmons J.C, Hublin T.J., Preparations and applications of synthetic linked azamacrocycle ligands and complexes. *Coordination Chemistry Review*, **254 (15-16)**: 1661 **(2010)**

29. Mishra S., Agarwal R., Singh A., Four novel classes of heterobimetallic isopropoxides of chromium(III). *Transaction Metal Chemistry*, **27(7)**: 712 **(2002)**

30. Baumgartner T., Régis Réau, Organophosphorus π-Conjugated Materials. *Chemical Review*, **106(11)**: 4681**(2006)**

31. Rade H.St., Temperature dependence of the magnetic susceptibility of mercury tetrathiocyanatocobalt. *J. Phys. Chem.*, **77:** 424 **(1973)**

32. Srivastava S., ESCA Studies of Metal Complexes. *Applied Spectroscopy Reviews*, **22**: 401 **(1986)**

33. Geary W.J., The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coordination Chem*., **7(1)**: 81 **(1971)**

34. Siddiqi Z.A., Mathew V.J., Synthesis of a novel 16-membered tetrapeptide macrocycle, dibenzo [c,k] [1,6,9,14]tetra-aza cyclohexadecane[2,5,10,13] tetraone. electrochemical evidence for the stability of +l oxidation state of cobalt and copper. *Polyhedron*, **13:** 799 **(1994)**

35. Matsuoka S., Yamamoto K., Ogat T., Kusaba M., Nakashima N., Fujita E., Yanagida S., Efficient and selective electron mediation of cobalt complexes with cyclam and related macrocycles in the p-terphenyl-catalyzed photoreduction of carbon dioxide. *Journal of American Chemical Society*, **15:** 601 **(1993)**

36. Colthup N.B., Dally L.H., *Stephen E., Wiberley* S.E., Introduction of Infrared and Reman spectroscopy, Academic Press, New Delhi. **(1964)**

37. Verma S., Singh D., Krishna V., Potentiometric Studies of Bivalent Metal Ions with Adenine and Nitrilotriacetic Acid. *Int. J. Res. Chem. Environ*., **6 (3):** 1 **(2016)**

38. Shakir M., Varkey S.P., Six-coordinate dinuclear hexaazamacrocyclic complexes of nickel(II), copper(II) and zinc(II) with tetraamide group ligands. *Transition Metal Chemistry*, **19(6)**: 606 **(1994)**