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Synthesis and characterization of Mn(II), Co(II), Ni(II) and Cu(II) complexes with Schiff bases derived from terephthalaldehyde and isophthalaldehyde

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الخلاصة

حضرت سلسلة من المعقدات الجديدة من النوع $[M_2LCl_4]$ و$[M_2L_2Cl_4]$ حيث M=Mn(II), Co(II), Ni(II) و Cu(II) وان $L=L^1$ او L^2 {L^1= 1،4- بس(3-امينو-1،2،4-ترايازول) ترفثايليدين و L^2= 1،3- بس (2-امينو بيريميدين) ايزوفثايليدين} بنسبة 1:2 و2:2 (L:M) وتم تشخيصها من خلال التوصيلية المولارية، العزوم المغناطيسية، أطياف الأشعة تحت الحمراء، الأطياف الالكترونية، طيف الرنين النووي المغناطيسي، التحليل الدقيق للعناصر C.H.N وتعيين المحتوى الفلزي.

أوضحت دراسة التوصيلية المولارية بمذيب DMF و DMSO ان جميع المعقدات غير الكتروليتية، كما بينت العزوم المغناطيسية والأطياف الالكترونية ان بعض المعقدات تمتلك الشكل رباعي السطوح والبعض الآخر يمتلك الشكل ثماني السطوح.

Abstract

A series of new complexes of the type $[M_2LCl_4]$ and $[M_2L_2Cl_4]$ where M=Mn(II), Co(II), Ni(II) and Cu(II), $L=L^1$ or L^2 {L^1= 1,4-Bis (3-amino-1,2,4-triazole) terephthylidene, L^2=1,3-Bis (2-amino pyrimidine) isophthylidene} have been prepared in 1:2 and 2:2 (L:M) molar ratio and characterized by molar conductance, magnetic moment, FT-IR,^{1}H-NMR, Uv-visble spectra studies and metal content analysis. Conductivity data in DMF and DMSO solution showed that all complexes are non-electrolyte.

Magnetic moment and electronic spectra indicate that some of the complexes have a tetrahedral and the others have an octahedral environment.

Introduction

The chemistry of transition metal complexes with Schiff base ligands is attracting increasing attention by chemists and has undergone a spectracular growth during the last few years due to their involvement in catalytic processes and discovery of proteins and enzymes which required two or more metal ions for their activity (1).

Schiff bases have remarkable property of forming binuclear complexes and serve as excellent chelating ligands(1-4). Schiff base metal complexes have broad applications and have been used as analytical reagents(5), catalysts (6) and showed anti-tumor(7), anti-viral(8), anti-fungal(9) and anti-bacterial(10) activities.

Schiff base complex of the type $[Cu_2(bpy)_2(PDIAla)(H_2O)_2](ClO_4)_2.H_2O$ where (H_2PDIAla=N,N'-(P-Xylene) dialanine, bipy=2,2'-bipyridine) have been prepared and the single x-ray diffraction technique indicate that each Cu(II) ion coordinate with N_3O_2 donor set and have distorted square pyramidal geometry(11), where Cu(I) ions in dinuclear complex $[Cu_2LX_2]$ derived from the condensation of 1,3-diaminopropane and benzene-1,3-dicarboxaldehyde in the presence of CuX($X=Cl^-,Br^-,I^{--}$) salt have distorted tetrahedral geometry by the coordination through two N_2X_2 donor sets(12).

Phesico-chemical studies of the complex $[Cu_2L(SCN)_2]$ derived from the condensation of 1,3-dicarboxaldehyde with 1,3-diaminopropane in the presence of $Cu(CH_3CN)_4ClO_4$ and KSCN salt indicate that each metal ion have distorted trigonal planer geometry(13). Therefore, it was of interest to investigate the coordination behavior of two Schiff bases derived from terephthalaldehyde and isophthalaldehyde with some divalent transition metal chlorides(13).

Experimental

All chemicals used were reagent grade from B.D.H or Fluka companies, used as supplied.

Melting point or decomposition temperature were determined on electrothermal 9300 melting point apparatus. IR spectra were recorded on Tensor 27 Brucker FT-IR spectrophotometer (400-4000 cm^{-1}) using KBr disc. Electronic spectra were recorded in DMF or DMSO (10^{-3}M) solutions on Shimadzu UV/V is recording UV-160 spectrophotometer at room temperature using 1cm quartz cell. Molar conductance were measured for 10^{-3}M solution in DMF and DMSO using a conductivity meter model PCM3-Jenway. magnetic susceptibility measurements of the complexes were carried out at 25 °C on the solid state, by Faraday' method using Brucker BM6 apparatus. Elemental analysis of the ligand and complexes were performed on Perkin Elmer 2400 analyzer at Al-al-Bayt University (Jordon). The metal content of complexes were determined spectrophotometrically using Shimadzu AA670 atomic absorption spectrophotometer, chloride was determined using the precipitation method (14).

^{1}HNMR spectra were recorded in DMSO-d_6 using Bruker 300 MHZ at Al-al-Bayt University (Jordon).

Synthesis of 1,4-Bis(3-amino-1,2,4-triazole) terephthyliden(L^1).

A clear solution of (3-amino-1,2,4-triazole) (1.68 g,0.02 mole) in methanol (10ml) was added slowly and drop wise to a solution of terephthalaldehyde (1.34g,0.01 mole) in methanol (10 ml), the mixture was stirred about 30min. Two drops of conc. Hydrochloric acid were added. The resultant solution was refluxed for 6h, after cooling, white precipitate was filtered off, washed with cold methanol and with diethylether then dried under vacuum.

Synthesis of 1,3-Bis(2-amino pyrimidine) isophthyliden(L^2).

It was prepared by using (1.9 g,0.02 mole) of 2-amino pyrimidine and (1.34 g,0.01 mole) of isophthyldehyde then applied the above procedure.

Preparation of [$M_2L^1Cl_4$] and [$M_2(L^1)_2Cl_4$] complexes

M=Mn(II),Co(II),Ni(II) and Cu(II),

The ligand L^1 (0.27g, 0.001 mole or 0.53g, 0.002 mole) was dissolved in 30 ml DMF in a 100ml round bottom flask. A solution of (0.002 mole) of metal salt [$MnCl_2.4H_2O$(0.39)g, $CoCl_2.6H_2O$(0.48g), $NiCl_2.6H_2O$ (0.48g) and $CuCl_2.2H_2O$(0.34g)]] in 10 ml of absolute ethanol was added drop wise for 10 min. period with continuous stirring at room temp. The mixture were refluxed for (2-3)h, after cooling the precipitate filtered off and washed with cold DMF and diethylether then dried under vacuum.

Preparation of [$M_2L^2Cl_4$], [$M_2(L^2)_2Cl_4$] complexes.

A solution of (0.002 mole) of metal salt [$MnCl_2.4H_2O$ (0.39g), $CoCl_2.6H_2O$ (0.48g), $NiCl_2.6H_2O$ (0.48g) and $CuCl_2.2H_2O$ (0.34g)] in 10 ml absolute ethanol was added drop wise for 10 min with continuous stirring to a hot solution of the ligand L^2(0.29g,0.001 mole or 0.58 g,0.002 mole), in 10 ml methanol, the precipitate was observed after about 10 min then the mixture was refluxed for 1h to complete the reaction, then it was filtered off, washed with hot methanol, ether and dried.

Results and Discussion

Direct reaction of ligand L^1 or L^2 with an ethanolic solution of metal (II) chloride in 1:2 or 2:2 molar ratio (L:M) gave (15) complex. In general all complexes are quite stable in dry air and decompose at a degree above 290°C, they are insoluble in most organic solvent but soluble in DMF or DMSO.

Some physical properties of ligands and their complexes are listed in (Table 1). The molar conductance in 10^{-3} M solution in DMSO for L^1 complexes and in DMF for L^2 complexes are in the range (11.14-17.05) and (9.68-18.35)$ohm^{-1}cm^2mol^{-1}$, respectively indicating a non-electrolytic nature of the complexes(10,15). This is consistent with the stoichiometry assumed for complexes on the basis of analytical data

^{1}H-NMR Spectra

The formation of Schiff base ligand L^2 and its complex (11) were observed by peak ratios in the ^{1}H-NMR spectra which was taken using DMSO-d_6 solvent. The spectra of ligand show one signal for 2 proton of (-CH=N) groups at δ=4.93 ppm while another signal for 10 protons of aromatic ring was observed at δ=7.292 ppm. In the complex the azomethin protons were shifted to appeared as a doublet at δ= 4.232 ppm and 4.427 ppm, while the aromatic protons were shifted and appeared as a multiplete in the range 7.22-7.48 ppm.

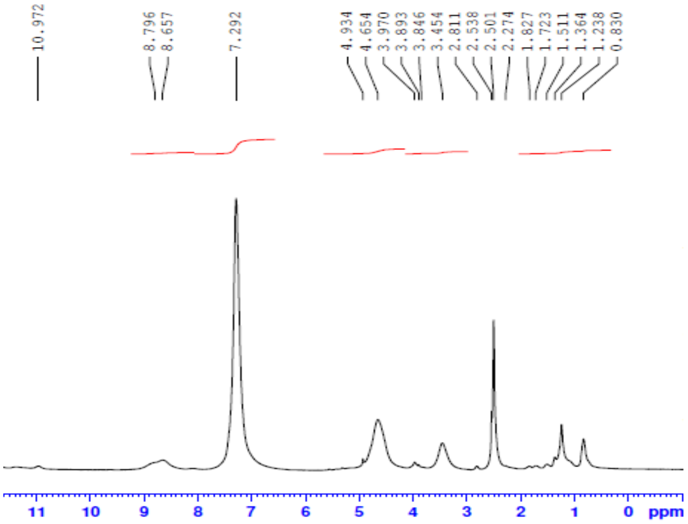


Fig (1): ^{1}H-NMR for (L^2)

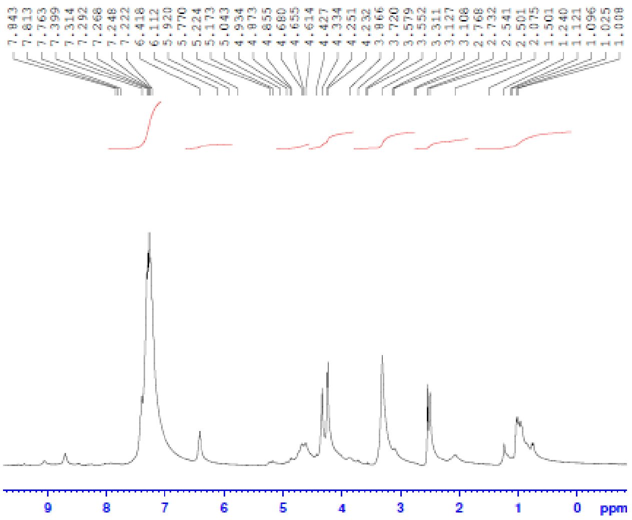


Fig (2): ^{1}H-NMR for complex(11) [$Cu_2L_2Cl_4$]

FT-IR spectra

The most important IR assignment of ligand and their complexes are listed in (Table 2). The ligands L^1 and L^2 show an intense band due to υ(C=N) of azomethine group at 1608 and 1597 cm^{-1} consistent with the iminic absorption of free Schiff bases(15,16). In all complexes this band undergoes a shift to higher frequencies and observed at (1631-1658 cm^{-1})(15,17), it may be due to increasing bond order of the C=N double bond on coordination with the metal ions as a result of electron donating of the other attached groups or due to the strain that occurred on the coordinating site on coordination(18), while the band at 1529 cm^{-1} and 1585 cm^{-1} which was assigned to υ(C=N) in triazole and pyrimidine ring of ligands was shifted to lower frequencies at (1495-1579 cm^{-1}) in spectra of complexes this suggest that the coordination take place also through the nitrogen of the ring to the metal ion(19,20), but there is no shift in this band of cobalt complex (13) indicate that the υ($C=N_{ring}$) dont shared in coordination.

The IR spectra of L^1 show bands at 3130cm^{-1} and 3151 cm^{-1} were assigned to symmetric and asymmetric stretching vibration of υ N-H(21) of trizole ring, in spectra of L^1 complexes these bands were almost unchanged forming the non-involvement of υ N-H group in coordination.

The ligand coordination is substantiated by new band appearing at the ranges (418-496 cm^{-1}) for the complexes, these are mainly attributed to υ(M-N)(3). All complexes show no band for M-Cl because it is below the spectro photometer limits.

Electronic spectra and magnetism

The magnetic moments and the electronic spectral data at 25°C of the ligands and their complexes are listed in (Table 3). The electronic spectra of ligand L^1 in DMSO (L^2 in DMF) show the aromatic intenses bands at 32894 cm^{-1} and 47619 cm^{-1} is attributed to benzene $\pi \longrightarrow \pi^*$ transition and at 31446 cm^{-1} and 32051 cm^{-1} due to the $n \longrightarrow \pi^*$ transition of the non-bonding electrons present on the nitrogen of the azomethine group, these transitions are also found in spectra of complexes but they are shifted, confirming the coordination of ligands to metal ions(3). The new intense band in spectra of all complexes at the region 22935-32065 cm^{-1} may be associated with the charge transfer transition(12).

The Mn(II) complexes (1,4,8,12) show magnetic moments at (5.71-6.10 B.M) which appreciably close to the calculated spin-only value for five unpaired electrons, and reveals high spin state. The electronic spectra of Mn(II) complexes show no prominent absorption that could be assigned for d-d transition. The d-d transition in Mn(II) octahedral complexes are doubly forbidden from the ^6A_1g towards the quartet terms $^4A_1g(G)$, $^4Eg(E)$, $^4T_2g(G)$, $^4T_1g(G)$ exhibit very small intensity and are concealed by the intraligand transitions, and in tetrahedral environment, these transitions are still spin-forbidden but no longer parity forbidden, these transitions are ~100 times stronger, there fore, structures of the prepared Mn(II) complexes(1,4,8,12) were proposed depending on the data of other measurements namely metal content and IR spectra(22).

The magnetic moment values of Co(II) complexes (2,9,13) were in the rang (4.26-4.88 B.M) indicating tetrahedral geometry(1), their electronic spectra exhibits one transition υ_3, $^4A_2(F) \longrightarrow {}^4T_1(p)$ consisting of two humps located at (14836-15455 cm^{-1}) and (16286-16447 cm^{-1}), the splitting of this band is expected due to distortion of Jahn-Teller type of the tetrahedral structure in the excited state(23), the other two bands υ_1 and υ_2 are below the spectrophotometer limits. The magnetic moment of Co(II) complex (5) were found to be 4.92 B.M, its electronic spectra showed bands at 10183,16339 and 19230 cm^{-1} assignable to $^4T_1g(F) \longrightarrow {}^4T_2g(F)$, $^4T_1g(F) \longrightarrow {}^4A_2g(F)$ and $^4T_1g(F) \longrightarrow {}^4T_1g(p)$ respectively, these observation indicating an octahedral geometry around Co(II) ions(24).

The magnetic moment of dinuclear Ni(II) complexes (6,14) were found to be 3.15 and 3.04 B.M. The electronic spectra of these complexes show three bands at the region (10131,10229), (18867,14577) and (22624-24038) assigned to $^3A_2g(F) \longrightarrow {}^3T_2g(F)$, $^3A_2g(F) \longrightarrow {}^3T_1g(F)$ and $^3A_2g(F) \longrightarrow {}^3T_1g(p)$ transition, respectively, this show that the Ni(II) ions having an octahedral geometry(15). The magnetic moment value of complex (10) found to be 3.94 B.M and its electronic spectra show a band υ_3 at 14792 cm^{-1} due to $^3T_1(F) \longrightarrow {}^3T_1(p)$ transition in tetrahedral geometry(1), the other two bands υ_1 and υ_2 are located in the lower section of the spectra, below the spectrophotometer limits.

The obtained magnetic moment values per Cu(II) ion at the range (1.73-1.82 B.M) corresponds to the presence of unpaired electron (25).

The electronic spectra of Cu(II) complexes (3,11) showed a broad band at 11467 and 10482 cm^{-1} attributed to $^2T_2 \longrightarrow {}^2E$ transition which is comparable with complexes having tetrahedral structure(26,27), while complexes (7,15) showed abroad absorption band at 15552 cm^{-1} and 15060 cm^{-1} arises from two or three d-d transition $^2B_1g \longrightarrow {}^2A_1g$, $^2B_1g \longrightarrow {}^2B_2g$ and $^2B_1g \longrightarrow {}^2Eg$ suggest that the Cu(II) ion exhibits octahedral geometry(28,29).

Conclusion

The ligands and their complexes were prepared and characterized by physio-chemical methods, in molar conductance of binuclear Mn(II), Co(II), Ni(II) and Cu(II) were non-electrolytic in nature. The spectroscopic data of metal complexes with nitrogen of azomethin group and nitrogen of the triazole and pyrimidine ring then L^1 and L^2 act as a tetradentate ligands and as bidentate ligand through azomethin group only in complex (13). Hence all complexes have been in tetrahedral or octahedral structure (Fig 1).

Table 1: Some physical properties and analytical data of the ligands and their complexes

NO.	Complexes	Color	m.p (°C)	Analysis calc.(Found)%			Cl%Calc. (found	M%Calc. (found)	Λm ohm^{-1} cm^{2}mol^{-1}
				C	H	N			
L^1	$C_{12}H_{10}N_8$	White	278-280	54.13(53.99)	3.78(3.62)	42.08(42.02)	---	---	---
1	$[Mn_2L^1Cl_4]$	Pale Yellow	365*	---	---	---	27.38(26.78)	21.21(20.83)	15.25
2	$[Co_2L^1Cl_4]$	Blue	335*	27.40(27.11)	1.91(1.59)	21.30(20.89)	26.96(26.11)	22.41(23.14)	14.35
3	$[Cu_2L^1Cl_4]$	Green	325*	---	---	---	26.50(25.83)	23.74(23.11)	11.40
4	$[Mn_2(L^1)_2Cl_4]$	Pale Yellow	366*	36.75(36.35)	2.57(2.37)	28.57(28.16)	18.08(17.32)	14.01(13.53)	15.25
5	$[Co_2(L^1)_2Cl_4]$	Dark green	322*	---	---	---	17.90(17.01)	14.87(14.19)	17.25
6	$[Ni_2(L^1)_2Cl_4]$	Pale Green	340*	---	---	---	17.91(17.25)	14.83(14.25)	11.14
7	$[Cu_2(L^1)_2Cl_4]$	Dark green	288*	35.96(35.53)	2.51(2.29)	27.96(27.81)	17.69(16.84)	15.85(15.77)	17.05
L^2	$C_{16}H_{12}N_6$	White	211-212	66.65(66.81)	4.19(4.64)	29.14(29.12)	---	---	---
8	$[Mn_2L^2Cl_4]$	Milkywihte	>370*	---	---	---	26.26(25.87)	20.34(20.27)	18.28
9	$[Co_2L^2Cl_4]$	Violate	293*	35.06(34.77)	2.20(1.85)	15.33(15.62)	25.88(25.12)	21.50(22.31)	18.35
10	$[Ni_2L^2Cl_4]$	Pale Yellow	330*	35.09(34.69)	2.20(1.93)	15.34(15.75)	25.90(25.27)	21.44(21.20)	9.68
11	$[Cu_2L^2Cl_4]$	Green	252*	34.48(33.90)	2.17(1.72)	15.08(15.39)	25.45(25.12)	22.80(22.11)	18.28
12	$[Mn_2(L^2)_2Cl_4]$	Milkywihte	360*	---	---	---	17.12(16.52)	13.26(13.89)	15.06
13	$[Co_2(L^2)_2Cl_4]$	Violet	348*	---	---	---	16.96(16.26)	14.10(13.62)	16.60
14	$[Ni_2(L^2)_2Cl_4]$	Pale yellow	368*	---	---	---	16.97(16.61)	14.04(13.69)	13.90
15	$[Cu_2(L^2)_2Cl_4]$	Green	243*	---	---	---	16.77(16.04)	15.02(15.46)	18.08

* = decomposition temperture

Table 2: Characteristic Infrared spectral data of the ligands and their complexes

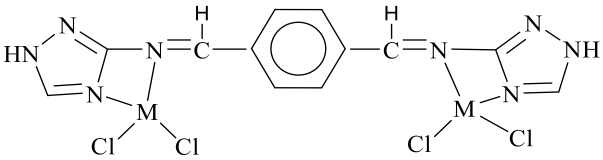
No.	Complexes	IR spectral bands (cm^{-1})		
		υ ($C{=}N_{imin}$)	υ ($C{=}N_{ring}$)	υ (M-N)
L^1	$C_{12}H_{10}N_8$	1608_S	1529_m	----
1	$[Mn_2L^1Cl_4]$	1658_S	1495_m	445_w,488_w
2	$[Co_2L^1Cl_4]$	1641_S	1510_m	458_w,476_m
3	$[Cu_2L^1Cl_4]$	1631_m	1520_m	478_w,496_m
4	$[Mn_2(L^1)_2Cl_4]$	1657_m	1498_m	466_m,484_m
5	$[Co_2(L^1)_2Cl_4]$	1658_S	1500_m	450_m,478_m
6	$[Ni_2(L^1)_2Cl_4]$	1649_S	1495_m	418_m,449_m
7	$[Cu_2(L^1)_2Cl_4]$	1651_S	1512_m	455_m,494_m
L^2	$C_{16}H_{12}N_6$	1597_S	1585_S	----
8	$[Mn_2L^2Cl_4]$	1651_S	1574_S	445_m,494_m
9	$[Co_2L^2Cl_4]$	1647_m	1576	450_m,482_m
10	$[Ni_2L^2Cl_4]$	1645_m	1577	418_m,448_w
11	$[Cu_2L^2Cl_4]$	1647	1572	418_w,472_w
12	$[Mn_2(L^2)_2Cl_4]$	1645_S	1576_S	430_m,474_m
13	$[Co_2(L^2)_2Cl_4]$	1645_S	1585_S	482_m
14	$[Ni_2(L^2)_2Cl_4]$	1643_m	1579_m	432_m,484_m
15	$[Cu_2(L^2)_2Cl_4]$	1651_S	1577	476_m,488_m

s=strong,m= medium, w=weak

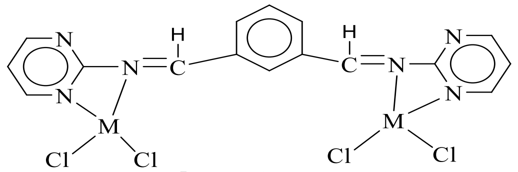
Table 3: Magnetic moments and the electronic spectral data of the ligands and their complexes

No.	Complexes	μ_{eff} (B.M)	assignment	Band maxima λ (cm^{-1})	Struct.
L^1	$C_{12}H_{10}N_8$	---	$n \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$	31446 32894	
1	$[Mn_2L^1Cl_4]$	5.71	C.T	28248	Td
2	$[Co_2L^1Cl_4]$	4.88	$^4A_2(F) \longrightarrow {}^4T_1(p)$ C.T	14925, 16286 29850	Td
3	$[Cu_2L^1Cl_4]$	1.73	$^2T_2 \longrightarrow {}^2E$ C.T	11467 31847	Td
4	$[Mn_2(L^1)_2Cl_4]$	5.83	C.T	26178	Oh
5	$[Co_2(L^1)_2Cl_4]$	4.92	$^4T_1g(F) \longrightarrow {}^4T_2g(F)$ $^4T_1g(F) \longrightarrow {}^4A_2g(F)$ $^4T_1g(F) \longrightarrow {}^4T_1g(p)$ C.T	10183 16339 19230 29411	Oh
6	$[Ni_2(L^1)_2Cl_4]$	3.15	$^3A_2g(F) \longrightarrow {}^3T_2g(F)$ $^3A_2g(F) \longrightarrow {}^3T_1g(F)$ $^3A_2g(F) \longrightarrow {}^3T_1g(P)$ C.T	10131 18867 22624 29239	Oh
7	$[Cu_2(L^1)_2Cl_4]$	1.78	$^2B_1g \longrightarrow {}^2A_1g$ $^2B_1g \longrightarrow {}^2B_2g$ $^2B_1g \longrightarrow {}^2Eg$ C.T	}15552 28409	Oh

No.	Complexes	μ_{eff} (B.M)	assignment	Band maxima λ (cm^{-1})	Struct.
L^2	$C_{16}H_{12}N_6$	---	$n \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$	32051 47619	
8	$[Mn_2L^2Cl_4]$	5.82	C.T	31450	Td
9	$[Co_2L^2Cl_4]$	4.34	$^4A_2(F) \longrightarrow {}^4T_1(p)$ C.T	14836, 16445 32051	Td
10	$[Ni_2L^2Cl_4]$	3.94	$^3T_1(F) \longrightarrow {}^3T_1(p)$ C.T	14792 30700	Td
11	$[Cu_2L^2Cl_4]$	1.80	$^2T_2 \longrightarrow {}^2E$ C.T	10482 22935	Td
12	$[Mn_2(L^2)_2Cl_4]$	6.10	C.T	32049	Oh
13	$[Co_2(L^2)_2Cl_4]$	4.26	$^4A_2(F) \longrightarrow {}^4T_1(p)$ C.T	15455,16447 30711	Td
14	$[Ni_2(L^2)_2Cl_4]$	3.04	$^3A_2g(F) \longrightarrow {}^3T_2g(F)$ $^3A_2g(F) \longrightarrow {}^3T_1g(F)$ $^3A_2g(F) \longrightarrow {}^3T_1g(P)$ C.T	10229 14577 24038 32065	Oh
15	$[Cu_2(L^2)_2Cl_4]$	1.82	$^2B_1g \longrightarrow {}^2A_1g$ $^2B_1g \longrightarrow {}^2B_2g$ $^2B_1g \longrightarrow {}^2Eg$ C.T	}15060 22935	Oh

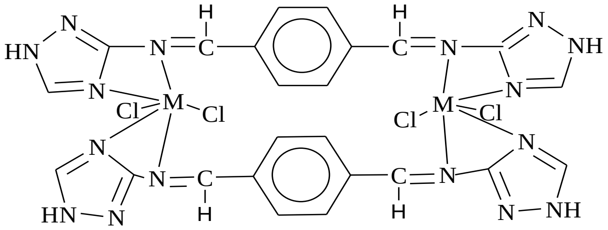


Complexes (1,2,3)
M=Mn(II),Co(II),Cu(II)
L=L^1



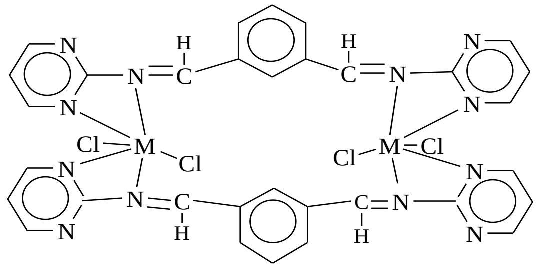
Complexes (8,9,10,11)
M=Mn(II),Co(II),Ni(II), Cu(II)
L=L^2

$[M_2LCl_4]$

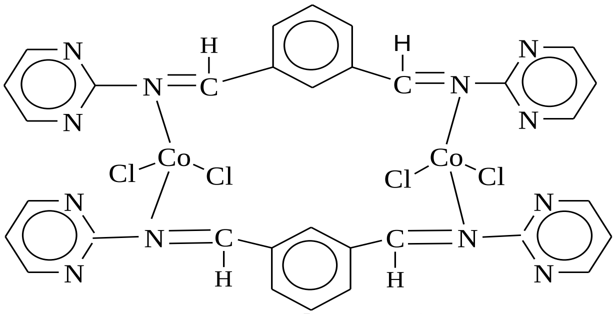


Complexes (4,5,6,7)
M=Mn(II), Co(II), Ni(II), Cu(II)
L=L^1

$[M_2L_2Cl_4]$



Complexes (12,14,15)
M=Mn(II), Ni(II), Cu(II)
L=L^2



Complexes (13)
$[Co_2(L^2)_2Cl_4]$

Fig 1: suggested structure of the complexes

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