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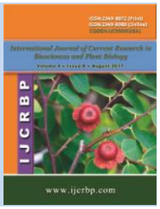

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Synthesis and Characterization of Some Transition and Non-Transition Metal Complexes with New Cyclic and Open Series Containing (N, O) as Donor Atoms

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Abstract

Transition and non transition metal ion complexes Mn(II), Fe(II), Co(II) , Ni(II), Cu(II), Zn(II), Cd(II) complexes with the L = N^1 , N^4 – bis (4-amino phenyl) succinamaide (L) from the reaction of p-phenylene di amine and diethyl succinate. Which the characterization of the ligand has been done on the basis of micro element analysis, infrared, spectra measurement. The complexes were characterized using IR, UV-Visible, molar conductivity, magnetic susceptibility, C.H.N.Cl analysis, IR spectra data suggest that the ligand was chelated with ionic metals via O(C=O) and N(NH_2) atoms. On the basis of physicochemical data as well as magnetic moment measurements, octahedral geometries were assigned for the complexes.

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Introduction

Macro cyclic compound are natural or synthetic polydentate ligands, having the donor atoms. They contain at least three donor atoms and the ring should have at least nine atoms (Lindoy, 1989). The macro cyclic ligand have been attracted, the interesting of the scientists because of their properties, such containing of more than donor atoms and the using of their complexes in different fields (Christensen et al., 1971; Akine et al., 2001). The synthesis of transition and non-transition metal macro cyclic complexes is a continuously developing area of investigation in inorganic and bio-organic chemistry (Beswick et al., 1996). The coordination chemistry of this type of the ligand was attracted the attention of the scientists, because of their role in application in different fields (Delgado, 1995). The earliest known examples of metal complexes of macro cyclic ligand were observed in natural substances, such as the porphyrin ring of the iron containing hem proteins (Lindoy, 1989; Melson, 1979; Goedken, 1979).

The preparation of some macro cyclic complexes containing nitrogen atoms with Ni(II) has been done as crown ethercomplexes (Lindoy, 1989). In this work the efforts were made to preparation of some complexes from the reaction of N^1,N^4 - bis (4-amino phenyl) succinamide (L)with[Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)] ions.

Materials and methods

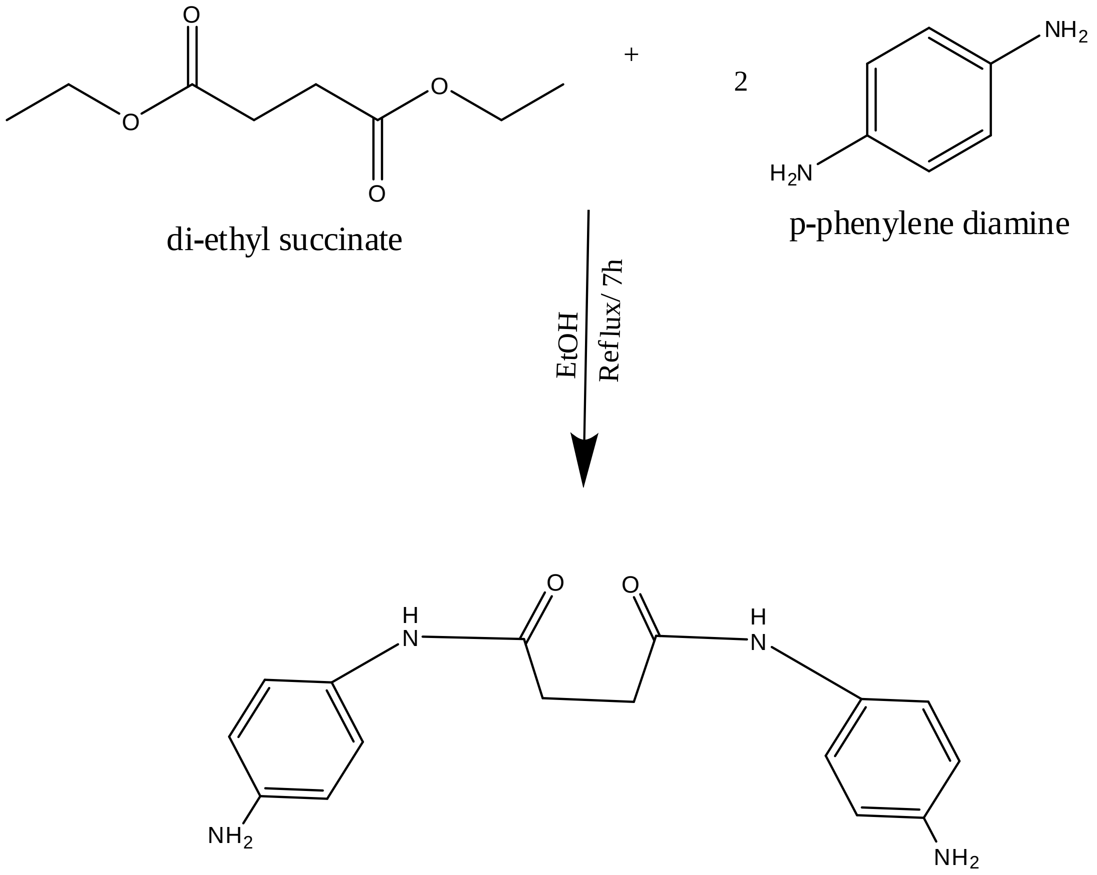
All chemicals used were either analytical grade or chemically pure. Conductivity measurement were carried out on 10^{-3} M solution of all complexes in DMF using (Conductivity Meter Model 4510 -JENWAY), IR Spectra were recorded on a Fourier-transform (FT.IR) spectra photo-meter, Tensor 27 Co. Bruker in the range 4000-400cm^{-1} using KBr discs.

The C.H.N analysis was carried out by Elemental Combustion System Costech Instrument (EC 4010) in Dicle University in Turkey, the electronic spectra for all complexes were recorded on Shimadzu UV-1650 PC UV-Visible Spectrophotometer (190-1100nm) using 10^{-3} M solution in DMF The magnetic measurement was measured at 25°C on the solids by faraday's method using broker B.M6 instrument, University of Mosul, Melting point was measured using Melting Point-Electro thermal 9300 Engineering LTD.

General procedure for the synthesis of the ligands

Synthesis of N^1, N^4 - bis (4-amino phenyl) succinamide (L):

A solid of P-phenylene diamine (2.16 g, 0.02 mole) was added to a solution of diethyl succinate (1.74 g, 0.01mole, 5.83 ml) in (10 ml) of ethanol, the mixture was refluxed for 7 hrs. The light brown precipitate was produced, filtered off, dried, washed with cold ethanol and re-crystallized from ethanol (Scheme 1).

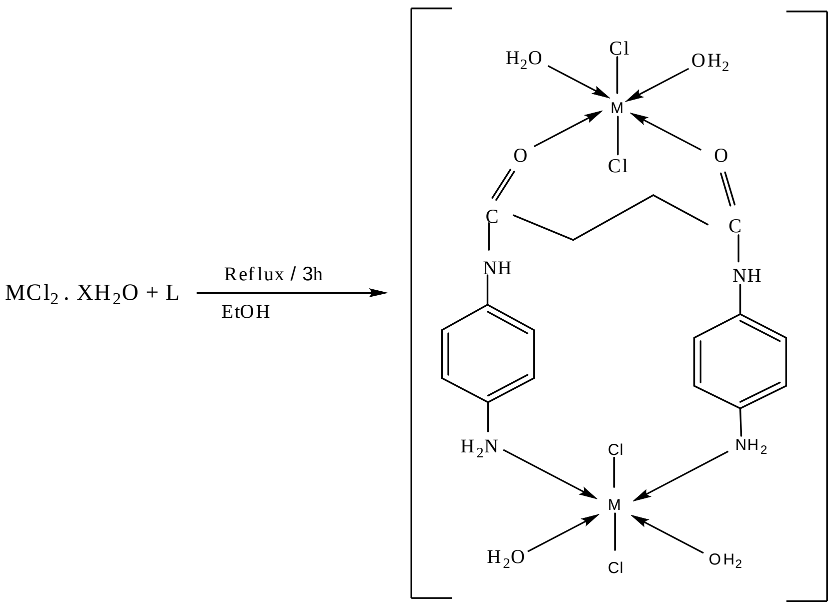


Scheme 1: Preparation of N^1, N^4-bis (4-aminophenyl) succinamide (L).

General procedure for the synthesis of metals complexes: $[M_2 (L_1) (H_2O)_4 Cl4]$

A solution salts (Z g, 0.001 mole) of MCl_2 .X H_2Oin hot ethanol (10ml) was added to a solution of (0.298 g, 0.001 mole) of L in (10ml) of ethanol.

The mixture was refluxed for 3 hrs to give colored precipitates, were filtered off, washed with ethanol, dried in oven at 80°C for 5 hrs (Scheme 2 and Table 1).



Scheme 2: Preparation of [M_2 (L_1)(H_2O)$_4$Cl4] complexes. M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II). X = (2-7)

Synthesis of [M_2(L) (γ-Pic)$_2$(H_2O)$_4$$Cl_2$]$Cl_2$:

To solution of [M_2(L)(H_2O)$_4$Cl4] (Zg , 0.001 mole) in (10 ml) hot ethanol (0.186 g, 0.002mol) of γ-Picolinein (5ml) of hot ethanol was added.

The mixture was stirred for 30 minutes to give colored complexes (Scheme 3 and Table 2).

Scheme 3: Preparation of [M_2(L) (γ-Pic)$_2$ (H_2O)$_4$ Cl_2] Cl_2 complexes M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II).

Table 1. Weight of metal salts of the prepared complexes.

Chemical Formula of salts	Weight Z(g)
$MnCl_2 . 4H_2O$	0.198
$FeCl_2 . 7H_2O$	0.234
$CoCl_2 . 6H_2O$	0.238
$NiCl_2 . 6H_2O$	0.238
$CuCl_2 . 2H_2O$	0.170
$ZnCl_2 . XH_2O$	0.244
$CdCl_2 . 2\ 1/2\ H_2O$	0.228

Table 2. Weight of $M_2(L)\ (H_2O)_4Cl_4$.

Chemical formula	Weight Z(g)
$[Mn_2(L)(H_2O)_4Cl_4]$	0.622
$[Fe_2(L)\ (H_2O)_4Cl_4]$	0.623
$[Co_2(L)(H_2O)_4\ Cl_4]$	0.630
$[Ni_2(L)(H_2O)_4Cl_4]$	0.629
$[Cu_2(L)(H_2O)_4\ Cl_4]$	0.639
$[Zn_2(L)\ (H_2O)_4\ Cl_4]$	0.643
$[Cd_2(L)(H_2O)_4\ Cl_4]$	0.737

Table 3. The physical properties of the prepared compounds.

Ligand No.	Chemical Formula	Molar conduct. $cm^2.ohm^{-1}.mol^{-1}$	M.P (°C)	Color	Selected IR(cm^{-1})				
					ν(NH)	δ(N-H)	$\nu(NH_2)$	ν(C=O)	(γ-Pic)
L	$C_{16}H_{18}N_4O_2$	----	137-139	Light Brown	3197(s)	1311(s)	3373(s)	1635(s)	-----
1	$[Mn_2(L)(H_2O)_4Cl_4]$	19	275*	Dark purple	3116(w)	1234(w)	3307(m)	1630(s)	-----
2	$[Fe_2(L)\ (H_2O)_4Cl_4]$	20	170-172	Brown Yellow	3128(w)	1290(s)	3327(s)	1628(m)	-----
3	$[Co_2(L)(H_2O)_4\ Cl_4]$	12	230*	Dark Green	3033(s)	1248(w)	3304(m)	1616(s)	-----
4	$[Ni_2(L)(H_2O)_4Cl_4]$	15	228-230	Green	3194(m)	1228(s)	3314(w)	1618(s)	-----
5	$[Cu_2(L)(H_2O)_4\ Cl_4]$	30	300 >	Brown Yellow	3177(w)	1167(w)	3362(w)	1633(s)	-----
6	$[Zn_2(L)\ (H_2O)_4\ Cl_4]$	5	200*	Pink	3182(s)	1244(s)	3273(s)	1628(m)	-----
7	$[Cd_2(L)(H_2O)_4\ Cl_4]$	30	180-182	Gray	3128(m)	1226(s)	3301(s)	1575(m)	-----
8	$[Mn_2(L)\ (H_2O)_4\ (\gamma\text{-}Pic)_2Cl_2]Cl_2$	131	240*	Dark Red	3185(w)	1246(m)	3371(w)	1628(m)	1616(s)
9	$[Fe_2(L)\ (H_2O)_4\ (\gamma\text{-}pic)_2Cl_2]Cl_2$	141	198-200	Brown	3175(m)	1178(m)	3368(m)	1634(s)	1618(s)
10	$[Co_2(L)\ (H_2O)_4\ (\gamma\text{-}pic)_2Cl_2]Cl_2$	143	200*	Green	3190(w)	1273(s)	3307(m)	1629(m)	1608(m)
11	$[Ni_2(L)\ (H_2O)_4\ (\gamma\text{-}Pic)_2Cl_2]Cl_2$	158	230*	Gray Green	3151(s)	1252(s)	3314(s)	1623(m)	1618(s)
12	$[Cu_2(L)\ (H_2O)_4\ (\gamma\text{-}pic)_2Cl_2]Cl_2$	135	182-184	Brown	3195(s)	1252(m)	3342(m)	1604(m)	1623(m)
13	$[Zn_2(L)\ (H_2O)_4\ (\gamma\text{-}pic)_2Cl_2]Cl_2$	147	220*	Pink	3140(m)	1213(s)	3269(s)	1633(s)	1618(s)
14	$[Cd_2(L)\ (H_2O)_4\ (\gamma\text{-}pic)_2Cl_2]Cl_2$	167	300*	Light Gray	3132(s)	1227(s)	3303(s)	1576(s)	1622(m)

*Decomposition , γ-Pic = (C=C) , (C=N)

Table 4. The % of C.H.N.Cl analysis for prepared compound, caluculed, (found).

Number	C%	H%	N%	Cl%
L	64.41 (64.38)	6.08 (6.04)	18.78 (18.71)	-----
1	-----	-----	-----	22.80 (22.55)
2	30.80 (30.77)	4.20 (4.14)	8.98 (8.92)	22.73 (22.43)
3	-----	-----	-----	22.51 (22.31)
4	30.52 (30.27)	4.16 (4.07)	8.90 (8.83)	22.52 (22.28)
5	-----	-----	-----	22.18 (22.01)
6	29.89 (29.82)	4.08 (3.98)	8.71 (8.66)	22.05 (21.87)
7	-----	-----	-----	19.24 (18.95)
8	-----	-----	-----	17.54 (17.35)
9	41.51 (41.39)	4.98 (4.91)	10.37 (10.30)	17.50 (17.32)
10	-----	-----	-----	17.37 (17.09)
11	-----	-----	-----	17.38 (17.15)
12	-----	-----	-----	17.18 (16.88)
13	40.55 (40.25)	4.86 (4.75)	10.13 (10.07)	17.10 (16.75)
14	-----	-----	-----	15.36 (15.14)

Results and discussion

$M_2(L)(H_2O)_4Cl_4]$ and $[M_2(L)(\gamma\text{-Pic})_2(H_2O)_4Cl_2]Cl_2$ were characterized using IR, UV – Vis , spectra , magnetic susceptibleted, molar conductivities measurements. The conductivity measurement in 10^{-3} M DMF at 25° suggesting the non electrolyte for (1-7) complexes and (1:2) electrolytic for (8-14) complexes.

Infrared spectral studies

The infrared spectrum of (L) ligand showed new bands in the range (3197, 3373 cm^{-1}) which are corresponding to ν(NH) (Keypour et al., 2002; Chandra and Kumar, 2005) and $\nu(NH_2)$ (Dolaz et al., 2001) amine. δ(N-H) appears at (1311cm^{-1}) (Chandra et al., 2004; Siddiqi et al., 2009), and the frequency assignable to ν(C=O) band at (1635cm^{-1}) (Dey and Ray, 1974; Aggarwal and Narang, 1973).

The position of ν(NH) stretching vibration has been shifted to lower frequencies in complexes while (γ-Pic) appears at (1608-1623cm^{-1}) indicating of coordination of N of γ-picoline with metal ions (Ibrahim et al., 2014) (Table 3).

Electronic spectra and magnetic measurements

The magnetic moment values for the Mn(II) complexes (1,8) have a magnetic moment values (5.85, 5.86 B.M) (Chandra et al., 2004; Ibrahim et al., 2014) while the electronic band at (31055, 32051, 28571, 37037)cm^{-1} referring to charge translation range, indicating octahedral geometries structure (Satpute et al., 2015; Kheiri et al., 1977).

The magnetic moment values for the Fe(II) complexes (2, 9) have a values (4.80, 4.91 B.M) (Shakir et al., 1995; Manzur, 1968) while the electronic band a (11235, 12820) cm^{-1} are attributed $^5T_2g \rightarrow {}^5Eg$ transition indicating octahedral structure (Shakir et al., 1995).

The magnetic moment for low spin Co(II) complex(3) has (2.48 B.M) value and electronic transition band at (14947) cm^{-1} which referring to ($^2Eg \rightarrow {}^2T_2g$). The data suggesting an octahedral geometrical for the complex (Kataoka and Kon, 1968).

The (high spin) Co(II) complex, (10) hasamagnetic moment value (4.85) (Nasman, 2001). The UV-Vis-Spectrum exhibits three bands at (10928, 14925, 18315) cm^{-1} which corresponding to (($^4T_1g(F) \rightarrow {}^4T_2g$), ($^4T_1g(F) \rightarrow {}^4A_2g$), ($^4T_1g(F) \rightarrow {}^4T_1g(p)$)) (Manzur, 1968).

According to mentioned data octahedral geometrical shape has been suggested for complex.

The magnetic moment values for the Ni(II) complexes (4,11) have a values (2.94, 3.06 B.M.) while three bands at (9389, 18656, 24509) cm^{-1}, (9541, 14814, 24271) cm^{-1}, ($^3A_2g \rightarrow \upsilon_1 {}^3T_2g$), ($^3A_2g \rightarrow \upsilon_2 {}^3T_1g$), ($^3A_2g \rightarrow \upsilon_3 {}^3T_1g(P)$)(18), transition indicating octahedral structure (Ibrahim et al., 2014).

The magnetic moment values for the Cu(II) complexes (5,12) have a magnetic moment values (2.11 , 1.94 B.M) (Saha and Gayen, 1983; Massey and Jahnson, 1975) electronic bands at (20325 , 16233 ,) cm^{-1} which are attributed to and $^2Eg \rightarrow {}^2T_2g$ transition indicating octahedral structure (Raman et al., 2010; Alaghaz and Ammar, 2010).

The µeff values of the two Zn(II) complexes were diamagnetic as expected and the µeff values of the two Cd(II) complexes were diamagnetic as expected (Raman et al., 2010; Kokamota and Hidaka, 1994; Al-Mogren and Alaghaz, 2013).

The conductivity measurements for all the complexes assist the structures which were non –conductive and 1:2 molar ratio (Table 3)

Conclusion

The present work includes the preparation of new ligand (L) and it's complexes with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) ions, where L=N^1, N^4- bis (4-amino phenyl) succinamide the characterization of the prepared compounds were carried out on the basis of IR,UV-Visible, spectra, molar conductivity, magnetic susceptibility and micro element analysis measurements. The results suggesting geometrical shapes for all complexes, in which of the ligand coordinates the metal ion via throw O(C=O) and N(NH_2).

Conflict of interest statement

Authors declare that they have no conflict of interest.

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