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Synthesis and characterization of mono and dinuclear Co(II),Ni(II),Cu(II) and Zn(II) complexes with dicarboxylic acid derivatives ligands

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Abstract: A new tetradentate carboxylic acid derivatives ligands, 1,4,8,11-tetraoxacyclo pentadecane-5,7,12,15-tetrone(L^1) and 1,4,9,12-tetra- oxacycloteptadecane,5,8,13,17-tetrone(L^2) were synthesized by condensation of 1,2-dibromoethane with disodium succinic acid or disodium glutaric acid. Their complexes with Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized and characterized by microanalysis, conductivity measurement FT-IR,UV-vis, metal content analysis and magnetic susceptibility measurements. The complexes have (1:1) or (2:1) metal to ligand stoichiometry. The spectral data revealed that the ligands acts as neutral bi and tetradentate, coordinating through the carbonyl oxygen atoms. All the complexes show magnetic moments corresponding to a high spin configuration except for zinc complexes. On the basis of spectral and magnetic measurements a four coordinated tetrahedral geometry may be assigned to these complexes.

Introduction

A self –assembly process involves the noncovalent interactions between two or more molecular subunit, mostly organics, forming a noncovalent molecular arrangement whose novel structure and properties are determined by the nature and positioning of the components involved(1). Coordinative frame works imply the involvement of metals in extended assemblies. The purpose of involving metals may be purely structural e.g., proving linkages or controlling network connectivity(2). Several studies in connection of the metal-organic frame works from noncovalent systems reveal that providing suitable conditions for the transfer of acidic protons to appropriate bases will result in increasing intermolecular interactions and stabilizing the resulting system. Furthermore carboxylic acids are tentative for coordination to metal centers by different coordinative modes. The metal carboxylates complexes are vastly studied(3-6), clearly indicate the fact that compounds with nultiple carboxylic acid groups are good target for supramolecular architechures and coordination polymers(7,8).

There new coordination compounds of Co(II),Cu(II) and Zn(II) based on different dicarboxylic acids formulated as (ACrH) [Cu(Pydc) (PydcH)].5H_2O(1).(2a-4mpH)$_2$[M(Pyzdc)$_2$ (H_2O)$_2$]. 6H_2O. M= Co(II) (2) and Zn(II)(3) have been synthesized and structurally characterized by elemental analyses , IR spectroscopy and single X-ray diffraction (where pydcH_2=pyridine-2,6-dicarboxylic acid,Acr=acridine, 2a-4mpy=2-amino-4methylpyridine, pyzdcH_2= 1,4-pyrazine-2,3-dicarboxylic acid). In all cases , the metal centers have distorted octahedral coordination geometries. Through hydrogen bonding or π-π staking interactions, 3D supramolecular networks are constructed in these complexes(9).The determined structure of the title compound $C_{24}H_{20}Ni_2N_8O_2$. Consist of the mononuclear trans-[Ni(Pyzdc)$_2$(H_2O)$_2$]$_2$. (Pyzdc=pyrazine-2,3-dicarboxylate). The Ni(II) atom is hexacoordinated by two (PyzdcH) groups and two water molecules. The coordinated water are in trans-diaxial positions and the (PyzdcH) anion acts as a bidentate ligands through O atoms of carboxylate group and the N atom of the pyrazine ring(10).

Mixed ligand complexes of Co(II),Ni(II),Cu(II) and Zn(II) have been investigated potentiometrically with pyridine-2,6-dicarboxylic acid (PDA) and 2-hydroxybenzalidine anthranilic acid (HBHA) in aqueous solution at 298.15 k and 313.15 k. the stability constant of these 1:1:1 ternary complex have been evaluated by the computational methods(11). In continuation of our research, here we wish to report have a study of the complexation behavior of Co(II),Ni(II),Cu(II) and Zn(II) ions with dicarboxylic acid derivative ligands.

Experimental

Material and Methods

Succinic acid and glutaric acid were purchased from AcROS and Fluka and used as received. All other chemical used were of reagent grade from Fluka and BDH chemical companies and used without any further purification. Doubly distilled deionized water was used in the procedure when needed.

Analyses of the ligands and their complexes were carried out using C.H.N.S elemental analyzer moded 2400 Perkin Elmer(AL-Abait University Jorden). The metal content was estimated spectrophotometrically using Shimadzu AA670 spectrophotometer, infrared spectra were recorded on FTIR Brucker Tensor 27Co spectrophotometer in the 200-4000 cm^{-1} range using CsI disc. Electronic spectra were obtained with Shimadza UV-Vis recording UV1650 spectrophotometer at room temperature , these measurement were recorded using a concentration of 10^{-3}M of the complexes in DMSO. The magnetic measurements were carried out at 25°C on the solid state by Farady's method using Bruker BM6 instrument. Conductivities were measured using conductivity meter model PCM3 Jenway. These measurements were obtained using DMSO over the 10^{-3}M solution of the complexes at 25°C. Synthesis of sodium salts of the dicarboxylic acid was carried out according to the Litretme method (12).

1) Synthesis of (L^1)

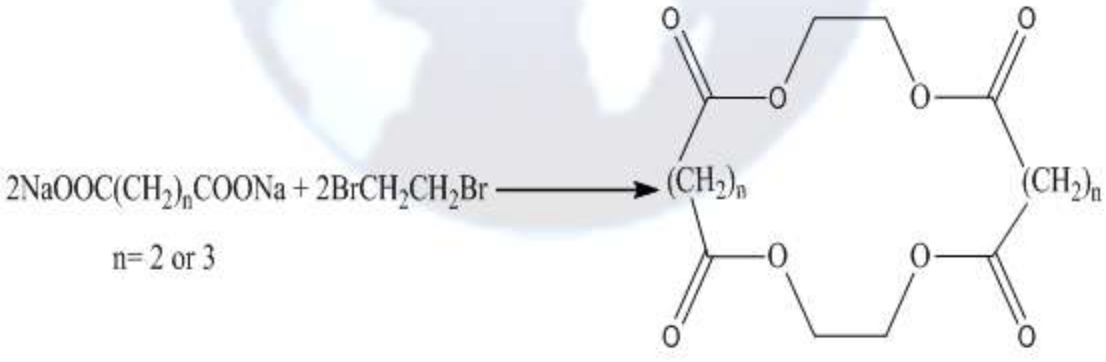
To (5.40g,0.02mol) of succinic acid disodium salt in 20 ml ethanol was added with stirring to a solution of 1,2-dibromo ethane (3.76g,0.02 mol) in 10 ethanol. The resulting mixture was stirred under reflux for 6hrs. a white precipitate was formed, the precipitate was washed several times by ethanol , water in order to remove the formed NaBr salts. Then the precipitate was washed with diethylether and dried in vacuum for several hours.

2) Synthesis of (L^2)

Glutaric acid disodium salt (3.32g,0.02mol) in 10 ml ethanol was added to a solution of 1,2-dibromomethane(3.76g,0.002mol) in 10 ml ethanol. The resulting solution stirred under reflux for 6 hrs.and the precedence was complexes as above.

Results and Discussion

The macrocyclic ligands (L^1 and L_2) has been prepared according to Scheme 1, and characterized by elemental analysis IR,U.V-Vis spectra and conductivity measurements.



Scheme 1: Preparation of (L_1 and L_2)

The reaction of the prepared ligands with Co(II),Ni(II),Cu(II) and Zn(II) in (1:1) and (2:1) molar ratio in ethanol gives $[M_2(L)Cl_4]$, $[M(L)Cl_2]$ complexes. All the metal complexes are colored solids and are stable towards air and have melting points(93-272°C). The complexes are insoluble in water and common organic solvents but are purely soluble in DMF and DMSO. The conductivity for 10^{-3}M solution of the complexes in DMSO show that all complexes are nonelectrolytic behavior(13) (Table 1). This is consistent with the stoichiometry of the complexes on the basis of analytical data. The IR spectral bands for the ligands and their complexes are given in Table 2. The IR spectrum of the free ligands are

characterized mainly by the strong bands at 1690-1710, 1280-1290 and 2960-2970 cm^{-1} which are attributed to the stretching frequencies of υ(C=O),υ(C-O) and υ(C-H) respectively.
The band at 1690-1710 cm^{-1} due to C=O stretching in the spectrum of the free ligands shifts lower were numbers from 20-50 cm^{-1} for L^1 and 25-41 cm^{-1} for L^2 in the metal complexes indicating that the carbonyl oxygen atoms are coordinated to the central metal ion(14). The band at 1280-1300 cm^{-1} due to C-O stretching in the spectrum of the ligands shift upper ward in all metal complexes. Further the IR spectra of the complexes of Co(II),Ni(II),Cu(II) and Zn(II) exhibit new bands at 480-550 and 290-330 cm^{-1} which may be assigned to υ(M-O) and υ(M-Cl) stretching modes respectively (15).

In order to obtain some information about the coordination properties of the metal complexes, the electronic spectra has been recorded as 10^{-3} M in DMSO and the results were listed in Table 2.The band observed at 31347-37037 cm^{-1} due to the ligands which may be assigned to (π-π*) or (n-π*) transition respectively.

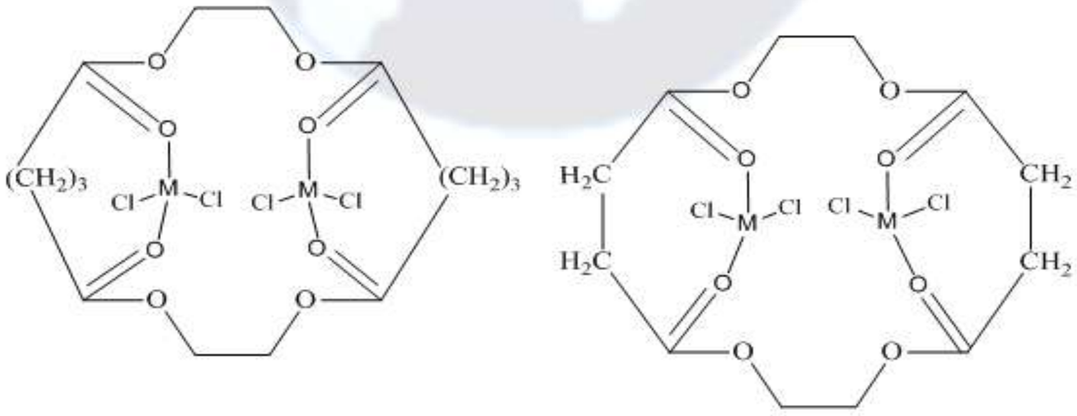
The spectrum of cobalt (II) complexes (1,5 and 9) show a bands at13698-16130cm^{-1} these bands are assigned to
$^4A_2(F) \longrightarrow {}^4T_1(p)(\upsilon_3)$ transition and a charge transfer at31446-37755 cm^{-1}, which consisting with proposed tetrahedral symmetry for these complexes(16).

The electronic spectra for Ni(II) complexes (2,6 and 10) the observed bands at14285-15220 cm^{-1} are due to
$^3T_1(F) \longrightarrow {}^3T_1(p)(\upsilon_3)$ transition in tetrahedral environment(17). In case of Cu(II) complexes (3,7 and 11) show a bands at14164-14310cm^{-1} were assigned to $^2T_2 \longrightarrow {}^2E$ transition in tetrahedral geometry(18).
The d^{10} electronic configuration of Zn(II) ions does not allow appreciations about the complex geometry on the bases of electronic spectra. Elemental analysis data, the bidentate or tetradentate type of ligands coordination and the nonelectrolytic nature of Zn(II) complexes allow us to suppose an tetrahedral surrounding.

The experimental magnetic moment for each metal complex are listed in Table 1. The magnetic measurement give an idea about electronic state of the metal ion in the complex. The magnetic moments for Co(II) complexes (1,5 and 9) are (4.59,4.73 and 4.40)B.M respectively which are typical for Co(II) ion in tetrahedral environment. The magnetic moment of Ni(II) complexes (2,6 and 10) are (3.41,3.23 and 3.25)B.M. the Cu(II) complexes (3,7 and 11) exhibit a value of (1.72,16.3 and 1.83) B.M, while Zn(II) complexes are diamagnetic . Based on elemental analysis data , magnetic susceptibilities measurement , molar conductivity determination and spectral studies (IR and UV-Vis) structural formula of the new complexes were proposed Fig 1.

Conclusion

New complexes of Co(II),Ni(II),Cu(II) and Zn(II) with the tetaoxyclco ligands resulted by the condensation between 1,2-dibromo ethane with disodium succinate of disodium glutarate were obtained. The IR spectroscopy and molar conductivity showed that, depending on the synthesis conditions of the complexes, the ligands as bidentate or tetradentate fashion. For all the complexes, the electronic spectra and the magnetic moment values suggest a tetrahedral geometry .



$M=Co^{+2},Ni^{+2},Cu^{+2}$ or Zn^{+2}

Fig 1: Suggested structures for the complexes

Table 1: Physical properties of the prepared ligands and their complexes

Seq.	compound	Color	m.p (°c)	Yield %	Analysis, found (calc.)%				μ_{eff}	(Λ) ohm^{-1}. cm^{2}. mol^{-1}
					C	H	O	M		
L^1	$(C_{12}H_{16}O_8)$	White	310^d	71	49.93(50.00)	5.43(5.55)	44.41(44.44)	---	---	12
1	$[Co(L^1)Cl_2]$	Violet	117-118	78	33.57(34.46)	3.49(3.82)	30.56(30.63)	13.98(14.09)	4.59	20
2	$[Ni(L^1)Cl_2]$	Light green	198-199	70	33.66(34.48)	3.46(3.83)	30.35(30.65)	13.87(14.05)	3.41	18
3	$[Cu(L^1)Cl_2]$	Dark blue	168-169	90	33.12(34.09)	3.55(3.78)	30.27(30.30)	14.93(15.03)	1.72	15
4	$[Zn(L^1)Cl_2]$	White	195-196	78	33.56(33.93)	3.26(3.77)	30.03(30.16)	15.14(15.41)	Dia	14
5	$[Co_2(L^1)Cl_4]$	Violet	93-94	79	25.98(26.29)	2.69(2.92)	23.18(23.37)	20.83(21.15)	4.73	10
6	$[Ni_2(L^1)Cl_4]$	Light green	171-172	65	25.63(26.31)	2.85(2.92)	23.10(23.39)	20.98(21.14)	3.23	12.5
7	$[Cu_2(L^1)Cl_4]$	Dark blue	236-237	71	25.33(25.86)	2.55(2.87)	22.86(22.98)	22.69(22.80)	1.63	25
8	$[Zn_2(L^1)Cl_4]$	White	270-272	78	25.32(25.68)	2.32(2.85)	22.68(22.83)	23.22(23.33)	Dia	21
L^2	$(C_{16}H_{24}O_8)$	White	330^d	75	55.56(55.81)	6.11(6.97)	37.09(37.20)	---	---	10
9	$[Co_2(L^2)Cl_4]$	Dark violet	125-126	66	31.22(31.81)	3.58(3.98)	21.05(21.20)	19.37(19.51)	4.40	20
10	$[Ni_2(L^2)Cl_4]$	Yellow	235-236	60	31.54(31.83)	3.81(3.97)	21.18(21.22)	19.32(19.46)	3.25	17
11	$[Cu_2(L^2)Cl_4]$	Dark green	223-226	72	31.20(31.33)	3.88(3.91)	20.76(20.88)	20.66(20.72)	1.83	14
12	$[Zn_2(L^2)Cl_4]$	White	198-200	70	31.01(31.13)	3.83(3.89)	20.59(20.76)	21.05(21.21)	Dia	10

d= decomposition temperature , dia= diamagnetic

Table 2: IR and electronic spectral data of the ligands and their metal complexes

No.	UV-Vis absorption bands (cm^{-1})	IR spectral bands (cm^{-1})				
		υ(C=O)	υ(C-H)	υ(C-O)	υ(M-O)	υ(M-Cl)
L^1	37037	1690_S	2970_w	1280_m	---	---
1	16130,31446	1650_S	2972_w	1304_m	495_m	325_w
2	143992,35971	1640_S	2970_w	1304_m	480_m	330_w
3	14164,36900	1660_S	2950_w	1283_m	500_m	290_w
4	30300	1652_S	2951_w	1285_m	502_m	295_w
5	13698,37735	1645_S	2949_w	1280_m	492_m	300_w
6	14285,36363	1655_S	2951_w	1293_m	534_m	310_w
7	14306,34364	1662_S	2950_w	1290_m	507_m	315_w
8	29720	1670_S	1949_w	1292_m	535_m	290_w
L^2	31347	1710_S	2960_w	1290_m	---	---
9	15220,31545	1685_S	2965_w	1300_m	537_m	290_w
10	15923,36363	1690_S	2960_w	1295_m	550_m	300_w
11	14310	2955_S	2955_w	1300_m	507_m	310_w
12	29000	2950_S	2950_w	1305_m	530_m	320_w

S= strong, m=medium, w= weak

References

[1]. Lehn J.M., Insteed J.W. and Atwood J.L.(Eds.),Supramolecular Chemistry, Wiely,Chichester, (2000).
[2]. Lehn J.M., Supramolecular Chemistry, New York,VCH, (1995).
[3]. Sharif M.A.,Aghabozorg H. and Moghim ,Acta Cryst., E63,1599, (2007).
[4]. Aghabozorg H.,Manteghi F. and Sheshmani S., J.Iran. Chem. Soc., 5, 184,(2008).
[5]. Aghabozorg H. and Khanlou E.,Acta Cryst.E63,m1753,(2007).
[6]. Aghabozorg H, Gasemikhah P.,Ghadermazi M.,Soleimannejad J. and Adams H.,Acta Crys.,E63,m1487,(2007).
[7]. Soleimannejad S.H.,Aghabozorg H.,Hooshmand S.,Ghadermazi M. and Gharamaleki J.A., Acta Cryst.,E63,m2022,(2007).
[8]. Aghajani Z.,Aghabozorg H.,Kanlou E.S.,Shokrollahi A.,Derki S. and Shamsipur M.,J.Iran.Chem.Soc.,6(2),373,(2009).
[9]. Mirzaci M.,Hosseini H.E.,Alfi N.,Aghaborg H.,J.A.,Kharasi H.R., Salimi A.R.,Shokorllahi A. and Aghaei R.,Struct. Chem.,22 (6), 1365,(2011).
[10]. Nikpour M.,Hosseini H.E.,Mirzaci M.,Necas M. and Alfi N., Bull.Chem.Soc.Ethiop,26(1),135,(2012).
[11]. Sinhh B. and Kumar D.,Inter.J.Sci.Res.Pub.,3(2),(2013).
[12]. Salvadores V.Leon,PhD Thesis,Dublin Institute of Technology. Irland.(2000).
[13]. Geary W.J.,Coord.Chem.Rev.,7,8,(1971).
[14]. Zheng B.,Zhang H.,Zhu H.,Luo S.,Lindoy I.F.,Memurtri J.C., Turner P. and Wei G.,J.Chem.Soc.Dalton Trans.,8,1349,(2005).
[15]. Nakamoto K.,Infrared of Inorganic and Coordination Compounds, John Weily, New York,(1997).
[16]. Buttrus N.H.,Yousif J.D. and Felman V.T.,Inter. J.Enhan.Res., Sci. Techn.& Eng.,3(3),54(2014).
[17]. Buttrus N.H.,Ahmed S.A. and Jameel W.M., Res.J. Chem. Sci., 3 (11),47,(2013).
[18]. Trifunovic S.R.,Markorix Z.,Saldic D.,Jekovic K.,Sabo Y. and Minic D.,J.Serb.Chem.Soc.,67,115,(2002).