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PİRİDİNKARBOKSİLİK ASİT TÜREVLERİ İLE BİPİRİDİN TÜREVLERİNİN METAL KOMPLEKSLERİ

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ÖZ

Bu çalışmada, literatürde yapılan piridindikarboksilik asit türevleri {2,3-piridindikarboksilik asit, 2,3-piridindikarboksilik asit *n*-oksit, 3,4-piridindikarboksilik asit, 3,5-piridindikarboksilik asit, 5-etil-2,3-piridindikarboksilik asitin, 2,4-piridindikarboksilik asit, 6-metil-2,4-piridindikarboksilik asit *N*-oksit, 2,5-piridindikarboksilik asit, 2,6-piridindikarboksilik asit, 4-hidroksi-2,6-piridindikarboksilik asit, 2,6-piridindikarboksilik asit *N*-oksit, 2,3,5-piridintrikarboksilik asit, 6-metil-2,3,5-piridintrikarboksilik asit, 2,4,6-piridintrikarboksilik asit, 2,3,5,6-piridintetrakarboksilik asit, 2,2’-bipiridin-3,3’,6,6’-piridintetrakarboksilik asit, 4,4’-bipiridin-2,2’,6,6’-piridintetrakarboksilik asit} ile bipiridin türevlerinin {2,2′-ditiyodipiridin, 4,4’-bipiridin, 4,4′-ditiyodipiridin, 1,2-bis(4-piridil)etan, 1,2-bis(piridin-4-il)eten, 1,2-bis(4-piridil)etilen, 1,3-di(4-piridil)propan, 1,2-bis(2,4-piridil)etan, 1,2,3,4-tetrakis(4-piridil)bütan, 4,4'-bipiridin *N*,*N*-dioksit, bis{2-(piridin-4-il)etenil}benzene, 4,4'-dipiridil-*N*,*N*'-dioksit, 1,2,4,5-tetrakis(4-piridil)benzene ve bis(4-piridil)amin} bazı metallerle {La(III), Mn(II), Co(II), Ni(II), Cu(I), Cu(II), Zn(II), Cd(II), Ag(I) Ru(II), In(III), Sn(II), Ga(III), La(III), Ce(III), Sm(III), Tb(III), Dy(III), Ho(III)} karışık ligandlı kompleksleri ve biyolojik aktiviteleri incelenmiştir. Literatürde piridindikarboksilik asit ve bipiridin türevlerinin anti oksidan, anti fungal, anti mikrobiyal, anti tümor, anti kanser, anti inflamatuar, anti ülser, anti diyabetik, analjezik ve radyoprotektif aktivite gibi biyolojik aktiviteleri vardır. Bu iki aktif grubun gösterdiği biyolojik özellikler, bunlardan elde edilecek olan proton transfer tuzu ve metal kompleksleri de benzer özelikler göstereceği aşikardır. Ancak metal kompleklserin aktivite çalışmaları oldukça azdır. Metal komplekslerinin biyolojik özelliklerin daha ayrıntılı bir şekilde çalışılması literature önemli bir katkı olacaktır.

Anahtar kelimeler: *Piridindikarboksilik asit, Bipiridin, Metal kompleksi.*

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METAL COMPLEXES OF PYRIDINCARBOXYLIC ACID DERIVATIVES AND BIPYRIDINE DERIVATIVES

ABSTRACT

In this study, complexes and biological activities of pyridindicarboxylic acid derivatives {2,3-pyridinedicarboxylic acid, 2,3-pyridinedicarboxylic acid n-oxide, 3,4-pyridinedicarboxylic acid, 3,5-pyridinedicarboxylic acid, 5-ethyl-2,3-pyridinedicarboxylic acid, 2,4-pyridinedicarboxylic acid, 6 -methyl-2,4-pyridinedicarboxylic acid N-oxide, 2,5-pyridinedicarboxylic acid, 2,6-pyridinedicarboxylic acid, 4-hydroxy-2,6-pyridinedicarboxylic acid, 2,6-pyridinedicarboxylic acid N-oxide, 2, 3,5-pyridinetricarboxylic acid, 6-methyl-2,3,5-pyridinetricarboxylic acid, 2,4,6-pyridinetricarboxylic acid, 2,3,5,6-pyridinetetracarboxylic acid, 2,2'-bipyridine-3,3 ', 6,6'-pyridinetetracarboxylic acid, 4,4'-bipyridine-2,2', 6,6'-pyridinetetracarboxylic acid} and bipyridine derivatives {2,2′-ditiyodipiridin, 4,4’-bipiridin, 4,4′-ditiyodipiridin, 1,2-bis(4-piridil)etan, 1,2-bis(piridin-4-il)eten, 1,2-bis(4-piridil)etilen, 1,3-di(4-piridil)propan, 1,2-bis(2,4-piridil)etan, 1,2,3,4-tetrakis(4-piridil)bütan, 4,4'-bipiridin *N*,*N*-dioksit, bis{2-(piridin-4-il)etenil}benzene, 4,4'-dipiridil-*N*,*N*'-dioksit, 1,2,4,5-tetrakis(4-piridil)benzene ve bis(4-piridil)amin} with mixed ligands with some metals {La(III), Mn(II), Co(II), Ni(II), Cu(I), Cu(II), Zn(II), Cd(II), Ag(I) Ru(II), In(III), Sn(II), Ga(III), La(III), Ce(III), Sm(III), Tb(III), Dy(III), Ho(III)} were investigated. In the literature, pyridindicarboxylic acid and bipyridine derivatives have biological activities such as anti oxidant, anti fungal, anti microbial, anti tumor, anti cancer, anti inflammatory, anti ulcer, anti diabetic, analgesic and radioprotective activity. It is obvious that the biological properties of these two active groups, the proton transfer salt and metal complexes obtained from them will also show similar properties. However, activity studies of metal complexes are very few. A more detailed study of the biological properties of metal complexes will be an important contribution to the literature.

Keywords: *Pyridindicarboxylic acid, Bipyridine, Metal complex.*

1. GİRİŞ

Organik asitlerden olan piridindikarboksilik asitler, yapısında iki -COOH grubundaki dört oksijen ve piridin halkasında bulunan elektron verici azot atomu içermektedir. 2,3-Piridindikarboksilik asit, 3,4-piridindikarboksilik asit, 3,5-piridindikarboksilik asit, 2,4-piridindikarboksilik asit, 2,5-piridindikarboksilik asit ve 2,6-piridindikarboksilik asit olmak üzere piridindikarboksilik asitlerin altı farklı izomeri vardır. Yapılan çalışmalarda piridindikarboksilik asitler metal iyonlarına ya metal merkezlerine karboksilat köprüsü ile bağlanarak dimerik veya polimerik kompleks oluşturdukları veya O, N, O’ uçlarından bir metal atomu ile şelat oluşturdukları gözlenmiştir. Piridinkarboksilik asit türevleri (H_2pka) ve proton vermiş formları (Hpka$^-$, pka^{2-}) ile birçok çalışma yapılmaktadır. Bu bileşikler antioksidan, antifungal, antimikrobiyal, antitümor, antikanser, antiinflamatuar, antiülser, antidiyabetik, antimütajen, süperoksit giderici ve radyoprotektif aktiviteye gibi biyolojik özelliklere sahiptir [1-6].

Bipiridiller, bipiridinler veya dipiridinler olarak adlandırılan bipiridin türevleri, iki piridin halkasının birbirini bağlanmasıyla oluşurlar. İki azot atomunun halkalara 2,2’-, 2,3’-, 2,4’-, 3,3’-, 4,4’- ve 3,4’-konumlara bağlanmasıyla altı izomeri vardır [7,8]. Bipiridin türevlerinin anti hipertansif, anti-bakteriyel, anti psikotik, kas gevşetici, analjezik, antioksidan, anti diyabetik, antiinflamatuar, anti

kanser, anti sıtma, enzım inhibisyonu, anti depresan, antikolinerjik gibi biyolojik aktiviteleri mevcuttur [9,10].

2. SENTEZLENEN METAL KOMPLEKSLERI

2,3-Piridindikarboksilik asit ($H_2$23pka) ile 4,4'-bipiridin'in proton transfer tuzu {(H_2bpy)(H23pka)$_2$} [11,12] ve Mn(III) {{(H_2bpy)[Mn(23pka)$_2$].(bpy).6H_2O}$_n$} [13], Cu(II) {{[Cu(H23pka)$_2$].2(bpy).6H_2O}$_n$ [14], [Cu(bipy)$_{0,5}$(23pka)].3H_2O, [Cu(bipy)$_{0,5}$(23pka)].0,5bipy.3H_2O [15], Zn(II) {[{Zn_2(2,3pka)$_3$}(H_2bpy).3H_2O]$_n$ [16], {[Zn(23pka)(2,2'-bpy)(H_2O)].2H_2O}$_n$ ve Cd(II) {{[Cd_2(23pka)(bpy)$_2$(NO_3)(H_2O)$_2$](NO_3).3H_2O}$_n$} [17], 1,2-bis(4-piridil)etan'ın (bpa) ile Cu(II) {{H_2bpa[Cu(μ-23pka)$_2$]}$_n$}, Cd(II) {[Cd(μ-23pka)(μ-bpa)$_{0,5}$(H_2O)$_2$]$_n$} [18] ve 2,3-piridindikarboksilik asit *N*-oksit ($H_2$23pkao) ile 4,4'-bipiridin'in Mn(II) {[Mn(23pkao)(bpy)(H_2O)$_2$]}, Co(II) {[Co_2(23pkao)$_2$(bpy)(H_2O)$_2$.H_2O]}, Cu(II) {[Cu(23pkao)(bpy).H_2O]} ve Zn(II) {[Zn_2(23pkao)$_2$(bpy)(H_2O)$_2$]} [19] kompleksleri sentezlenmiş ve yapıları çeşitli spektroskopik çalışmalar ile aydınlatılmıştır.

3,4-Piridindikarboksilik asit ($H_2$34pka) ile 1,2-bis(4-piridil)etilen'in (bpe) Co(II) {[Co_2(μ$_4$-34pka)$_2$(μ-bpe)(H_2O)$_2$].H_2O}$_n$} [18] ve 3,5-piridindikarboksilik asit ile 4,4'-bipiridin'in Sn {[(n-Bu_3Sn)$_2$(μ-35pka)(μ-bpy)]$_n$} [20] kompleksleri sentezlenmiş ve yapıları çeşitli spektroskopik metotlar ile açıklanmıştır.

5-Etil-2,3-piridindikarboksilik asitin (H_2Et23pka) ile 4,4'-bipiridin'in Co(II) {{[Co_2(Et23pka)$_2$(bpy)(H_2O)$_2$].3H_2O}$_n$}, 1,2-di(4-piridil)etilen'nin (bpe) Co(II) {{[Co_2(Et23pka)$_2$(bpe)(H_2O)$_2$].3H_2O}$_n$} [21] ve Zn(II) {[Zn_3(Et23pka)$_2$(HEt23pka)$_2$(bpe)]$_n$} [22], 1,2-bis(4-piridil)etan'ın (bpa) Co(II) {[Co_2(Et23pka)$_2$(bpa)(H_2O)$_2$].3H_2O} [23] ve Zn(II) {[Zn_3(Et23pka)$_2$(HEt23pka)$_2$(bpa)]$_n$} [22] ve 1,3-di(4-piridil)propan'ın (bpp) Zn(II) {{[Zn_2(Et23pka)$_2$(bpp)$_2$].H_2O}$_n$} kompleksleri sentezlenmiş ve yapıları çeşitli spektroskopik çalışmalar ile karakterize etmişlerdir.

2,4-Piridindikarboksilik asit ($H_2$24pka) ile 4,4'-bipiridin'in Co(II) {[(2,4pka)Co(bpy)Co(2,4pka)].2H2O} [24], Cu(I)/Cu(II) {[CuI_2CuII(bpy)$_2$(24pka)$_2$].4H_2O} [25], Zn(II) {[Zn_2(24pka)$_2$(bpy)(H_2O)$_4$].2H_2O [26], [Zn_2(24pka)$_2$(bpy)(H_2O)$_6$].2H_2O [27]}, 1,2-bis(4-piridil)etan Mn(II) {[Mn_2(24pka)$_2$(bpe)(H_2O)$_6$].2H_2O} [28], 1,2-bis(2,4-piridil)etan (bpa) Co(II) {[Co_2(24pka)$_2$(bpa)(H_2O)$_6$](H_2O)$_2$} [29], 2,2′-ditiyodipiridin'in (ald) Cu(II) {[Cu_2(24pka)$_2$(ald)$_2$(H_2O)$_2$].8H_2O} [30] ve 2,4-piridindikarboksilik asit *N*-oksit ($H_2$24pkao) ile 4,4'-bipiridin'in Co(II) {[Co(24pkao)(bpy)(H_2O)(H_2O)]$_n$}, Ni(II) {[Ni(24pkao)(bpy)(H_2O)(H_2O)]$_n$}, 6-metil-2,4-Piridindikarboksilik asit *N*-oksit (H_2M24pkao) ile 1,2,3,4-tetrakis(4-piridil)bütan'ın (tpb) Co(II) {[Co(M24pkao)(tpb)$_{0,5}$(H_2O)(H_2O)$_x$]$_n$}, Ni(II) {[Ni(M24pkao)(tpb)$_{0,5}$(H_2O)(H_2O)$_x$]$_n$}, Zn(II) {[Zn(M24pkao)(tpb)$_{0,5}$(H_2O)(H_2O)$_x$]$_n$}, Cd(II) {[Cd(M24pkao)(tpb)$_{0,5}$(H_2O)(H_2O)$_x$]$_n$} [31] ve Zn(II) {[Zn(M24pkao)(tpb)(H_2O)(H_2O)]$_n$} [32] kompleksleri sentezlenmiş ve yapıları çeşitli spektroskopik metotlar ile aydınlatılmıştır.

2,5-Piridindikarboksilik asit ($H_2$25pka) ile 4,4'-bipiridin'in Fe(II) {[Fe(25pka)(bpy)].H_2O [33], [Fe(25pka)(bpy)].H_2O [34]}, Co(II) {[Co(25pka)$_2$(H_2O)$_2$](H_2bpy) [35], {[Co_2(25pka)(25Hpka)$_2$(bpy)(H_2O)$_3$].6H_2O}$_\infty$ [36], [Co_2(bpy)(25pka)$_2$(H_2O)$_6$]$_n$ [37]}, Ni(II) {[Ni_2(bipy)$_{1,5}$(25pka)$_2$(H_2O)$_2$].3,5H_2O} [38], Zn(II) {(H_2bpy)[Zn(25pka)$_2$(H_2O)$_2$] [39], [Zn_2(25pka)$_2$(bpy)(H_2O)$_8$] [40]}, Sn {[(n-Bu_3Sn)$_2$(μ-26pka)(μ-bpy)]$_n$} [20], In(III)

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{{[Hbpy][In(H25pka)(H_2O)Cl_3].2H_2O}n, {[H_2bpy]$_4$[In_2(25pka)$_7$(H_2O)].7H_2O}n, {[H_2bipy]$_3$[In_2(25pka)$_6$(H_2O)].6H_2O}n} [41], 4,4'-bipiridin *N,N*-dioksit'in (bpyo) In(III) {[In_2(25pka)2(bpyo)(H_2O)$_2Cl_2$].2H_2O}$_n$} [42], Co(II) {[Co(2,5-pydc)(bipyo)$_{0,5}$(H_2O)$_3$·3H_2O]$_n$} [43] ve 1,2-di(4-piridil)etan Cu(II) {[Cu_2(25pka)$_2$(bpa)(H_2O)$_2$].3H_2O.DMF, [Cu_2(25pka)$_2$(bpa)(H_2O)$_2$].7H_2O} [44], 4,4′-ditiyodipiridin'in (ald-4) Cu(II) {{[Cu_2(25pka)$_2$(ald-4)(H_2O)$_2$].3H_2O.MeOH}$_n$} [45] kompleksleri sentezlenmiş ve yapıları çeşitli spektroskopik çalışmalar ile açıklanmıştır.

2,6-Piridindikarboksilik asit ($H_2$26pka) ile 4,4'-bipiridin'in Sr {(H_2bpy)[Sr(26pka)$_2$(H_2O)$_3$].3H_2O} [46], V(V) {[(H_2bpy)$_{0,5}$][VO_2(26pka)].2H_2O} [47], V(VI) {[(26pka)VO_2]$_2$(bpy).4H_2O} [48], Cr(III) {(H_2bpy)[Cr(26pka)$_2$].4H_2O} [49], Mn(II) {[Mn(bpy)$_2$(H_2O)$_4$](26pka).4H_2O} [50], Mn(III) {(H_2bpy)[Mn(26pka)$_2$].4H_2O,} [51] , Fe(II) {[Fe(bpy)$_2$(H_2O)$_4$](26pka).4H_2O} [52], Fe(III) {(Hbpy)[Fe(26pka)$_2$].4H_2O} [53,54], Co(II) {[Co_2(26pka)$_2$(μ-bpy)(H_2O)$_4$].4H_2O [54], [Co(bpy)$_2$(H_2O)$_4$](26pka).4H_2O [55], {[Co(26pka)(bpy)]·(MeOH)}$_n$ [56], [(26pka)Co(μ-bpy)Co(26pka)].8H_2O [57], [Co(26pka)(bpy)].0,5MeOH [58], [Co(26pka)(bpy)].0,5MeOH [55], {{[{Co(μ-26pka)}(μ-bpy)].3H_2O}$_\infty$, {[{Co(μ-26pka)}(μ-bpy)].H_2O.MeOH}$_\infty$, {[{Co(μ-26pka)}(μ-bpy)].2H_2O.0,5Me_2SO}$_\infty$, {[{Co(26pka)(OH_2)$_2$}$_2${μ-bpy}]·3H_2O}$_\infty$, {[{Co(26pka)(OH_2)$_2$}$_2${μ-bpy}].4H_2O}$_\infty$} [59], {[Co_3(O26pka)$_2$(bipy)$_2$(H_2O)$_4$].16/3H_2O}$_n$, {[Co(HO26pka)(bipy)].19/6H_2O}$_n$, {[Co(bipy)(H_2O)$_4$][Co(HO26pka)$_2$].1/2(bipy).4H_2O}$_n$, ve [Co_2(HO26pka)$_2$(bipy)(H_2O)$_4$].2H_2O} [60], {(H_2bpy)[Co(26pka)$_2$]·6H_2O, [(Hbpy)(H_2bpy)$_{0,5}$[Co(26pka)$_2$].3(23dhn)$_{0.3}$(H_2O)]$_2$, (H_2bpy)[Co(26pka)$_2$].3(27dhn)$_{0.6}$(H_2O), (Hbpy)$_2$[Co(26pka)$_2$]·(phgl)$_{0.5}$(H_2O) 2,3- or 2,7-dihidroksinaftalin ve florogüsinol} [61], Ni(II) {[Ni(26pka)(bpy)(μ-bpy)]$_4$·8H_2O [54], [Ni_2(26pka)$_2$(μ-bpy)(H_2O)$_4$].4H_2O} [62], [Ni_2(26pka)$_2$(bpy)(H_2O)$_4$].4H_2O [63], {[Ni(26pka)(μ-bpy)$_{1.5}$].H_2O.Me_2SO}$_\infty$ [59], Cu(II) {[{Cu(26pka)(H_2O)}$_2$(μ-bpy)].2H_2O [64], {Cu_2(26pka)$_2$(bpy)(H_2O).3H_2O}$_2$ [65], {Cu_2(26pka)$_2$(bpy).4H_2O}$_n$ [66], {[Cu_3(26pka)$_3$(bpy)$_{1,5}$(H_2O)$_{2,25}$].2,5(H_2O)}$_n$ [67], 2Cu_2(H_2O)$_2$(bpy)(26pka)$_2Cu_2$(H_2O)(bpy)(26pka)$_2$.6H2O, {[{Cu(26pka)}$_2$(μ-bpy)].2H_2O.CH_2Cl_2}$_\infty$ [68], [Cu_2(26pka)$_2$(bipy)].4H_2O, [{Cu(26pka)(OH_2)}(μ-bpy$_{0,5}$][{Cu(26pka)(OH_2)$_{0,75}$($OHMe$)$_{0,25}$}(μ-bpy){Cu(26pka)(OH_2)}].2,25H_2O.0,5MeOH, [69], Zn(II) {[Zn_2(HO26pka)$_2$(bipy)(H_2O)$_2$], {[Zn_2(HO26pka)$_2$(bipy)].2H_2O}$_n$ [60], {[Zn_2(26pka)$_2$(bpy)(H_2O)$_2$].5H_2O}$_n$} [70], [H_2bpy][Zn(26pka)$_2$].6H_2O, [H_2bpy][Zn(26pka)$_2$].3,5(4np).2H_2O (4np = 4-nitrofenol), [H_2bpy][Zn(26pka)$_2$].2(2,7dhn).5H_2O, [H_2bpy][Zn(26pka)$_2$].2(pyrogl).6H_2O (pyrogl = pirogallol) [71], Ga(III) {(H_2bpy)$_{1/2}$($H_2$26pka)$_{1/2}$[Ga(26pka)$_2$].4H_2O} [72] (H_2bpy)[Ga(26pka)$_2$].($H_2$26pka).4H_2O} [73], Sn {[(n-Bu_3Sn)$_2$(μ-25pka)(μ-bpy)]$_n$} [10], La(III) {(H_2bpy)$_{1,5}$[La(26pka)$_3$].2(cat).4H_2O, (H_2bpy$_3$[La(26pka)$_3$]$_2$.3(23dhn).19H_2O, (H_2bpy)$_{1,5}$[La(26pka)$_3$].3(27dhn).10H_2O [cat = 1,2-dihidroksibenzen, 23dhn = 2,3-dihidroksinaftalin, 27dhn = 2,7-dihidroksinaftalin]} [74], Ru(II) {[{(26pka)(COD)Ru}$_2$(μ-bipy)] (COD = 1,5-siklooktadien)} [75], In(III) {In_2Cl_4(26pka)(bpy)$_2$} [76], Ce(III) {{(H_2bp)[Ce_2(26pka)$_4$(H_2O)$_4$].5H_2O}$_n$} [77], Ce(IV) {(H_2bpy)[Ce(26pka)$_3$].4H_2O [78], Sn(II) {[Sn_2(H26pka)$_2$(H_2O)$_2O$]$_n$}, Pb(II) {(H_2bpy)$_{0,5}$[Pb(26pka)$_2$(Hbpy)].bpy.4H_2O} [79], Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Er(III), Yb(III) {[Ln(26pka)$_3Cu^I_3$(bipy)$_3$·m(H_2O)]$_n$ (Ln = Pr, Nd, m = 5; Ln = Sm, Eu, Gd, Tb, Er, Yb, m = 4)} [80], Hg(II) {[H_2bpy]$_2$[Hg(26pka)$_2$]$_2$·Hg(H_2O)$_2$(H26pka)$_2$.12H_2O} [81], Sm(II), Eu(II), Gd(II), Tb(II), Dy(II) {[{Ln_2(SO_4)$_2$(H_2O)$_2$(26pka)$_2Cu_2$(bpy)$_2$.2(H_2O)}]$_n$ (Ln = Sm, Eu, Gd, Tb, Dy)} [82], Sb(III) {(Hbpy)$_2$[Sb(26pka)(OH)$_2$(μ-OH)]$_2$.8H_2O} [83], UO_2 {(UO_2)$_2$(μ$_2$-OH)(26pka)$_2$Zn(bpy)(OAc)$_2$(H_2O)$_9$} [84] kompleksleri sentezlenmiş ve yapıları çeşitli spektroskopik metotlar ile karakterize etmişlerdir.

2,6-Piridindikarboksilik asit ($H_2$26pka) ile 1,2-bis(piridin-4-il)eten'in (bpe) Cu(II) {[{Cu(26pka)(OH_2)}(μ-bpe){Cu(26pka)}]·3H_2O, [Cu_2(26pka)$_2$(bpe)]·2H_2O}, 1,4-bis{2-(piridin-4-il)etenil}benzen'in (bpeb) Cu(II) {[Cu_2(26pka)$_2$(bpeb)].4H_2O, [{Cu(26pka)(OHMe)}$_2$(μ-bpeb)]} [69], 4,4'-dipiridil-*N*,*N*'-dioksit'in (dpypo) Cu(II) {[Cu_2(26pka)$_2$(dpyo)(H_2O)$_2$]$_n$}, 1,3-bis(4-piridil)propan'ın (bpp) Cu(II) {{[Cu_2(26pka)$_2$(bpp)(H_2O)$_2$].2H_2O}$_n$}, 1,2,4,5-tetrakis(4-piridil)benzen'in (bztpy) Ag(I) {[Ag_3(26pka)(μ-26pka)$_{0,5}$(bztpy)$_2$].3EtOH.6H_2O} [85], bis(4-piridil)amin'in Ce(IV) {(H_2bpa)[Ce(26pka)$_3$].3,5H_2O} [78] ve 1,3-bis(4-piridin)propan'ın (bpp) Zn(II) {[H_2bpp][Zn(26pka)$_2$].5H_2O, [H_2bpp][Zn(26pka)$_2$].4(2,7dhn).3H_2O (2,7dhn = 2,7-dihidroksinaftalin), [H_2bpp][Zn(26pka)$_2$].2(2,6dhn).8H_2O (2,6dhn = 2,6- dihidroksinaftalin)} [71] kompleksleri sentezlenmiş ve yapıları çeşitli spektroskopik çalışmalar ile aydınlatılmıştır.

4-Hidroksi-2,6-piridindikarboksilik asit (H_3O26pka) ile 4,4'-bipiridin'in Mn(II) {{[Mn_2(HO26pka)$_3$(H_2bpy)].5H_2O}$_n$ [86], [Mn_3(HO26pka)$_3$(H_2O)$_7$].bpy.3H_2O, [Mn_2(HO26pka)$_2$(bpy)(H_2O)$_2$].4H_2O [87]}, Co(II) {[Co_3(HO26pka)$_3$(H_2O)$_7$].bipy.3H_2O} [88], Cu(II) { [Cu_2(HO26pka)$_2$(bpy)(H_2O)$_2$].4H_2O, [Cu_2(HO26pka)$_2$(bpy)(H_2O)$_2$] [39], (H_2O)(O26pka)Cu(bpy)Cu(O26pka)(H_2O) [89],{[Cu(HO2,6pka)(bpy)$_{0,5}$(H_2O)].2H_2O}$_n$ [90]}, Zn(II) {[Zn(HO26pka)(H_2O26pka)$_2$].bpy.3,5H_2O}$_n$ [39], [Zn(HO26pka)(bpy)$_{0,5}$].H_2O}$_n$ [91], [Zn_2(HO26pka)$_2$(bpy)].2H_2O [92], Zn_2(bpy)(O26pka)$_2$(H_2O)$_2$].4H_2O [93]},Ga(III) {(H_2bpy)[Ga(HO26pka)$_2$]$_2$.7H_2O} [73], Sb(III) {(H_2bpy)[Sb_2(O26pka)$_2$(OH)$_2$(H_2O)$_2$].2H_2O} [94], Y(III) {(bpy)[Y(HO26pka)(H_2O26pka)(H_2O)$_2$].3H_2O], Er(III) {(bpy)[Er(HO26pka)(H_2O26pka)(H_2O)$_2$].3H_2O], La(III) {(bpy)[La(HO26pka)(H_2O26pka)(H_2O)$_2$].4,5H_2O], Sm(III) {(bpy)[Sm(HO26pka)(H_2O26pka)(H_2O)$_2$].4,75H_2O], Pr(III) {(bpy)[Pr(HO26pka)(H_2O26pka)(H_2O)$_2$].4,75H_2O} [95], 1,2-bis(4-piridil)etan'ın Cu(II) {{[Cu(HO26pka)(L)$_{0,5}$(H_2O)].2H_2O}$_n$}, 1,2-bis(4-piridil)eten'in Cu(II) {{[Cu(HO26pka)(L)$_{0,5}$(H_2O)].2H_2O}$_n$} ve 1,3-bis(4-piridil)propan'ın Ni(II) ve Cu(II) {{[M(HO26pka)(L)(H_2O)]·2H_2O}$_n$} [90] kompleksleri sentezlenmiş ve yapıları çeşitli spektroskopik metotlar ile açıklanmıştır.

4,4'-bipiridin'in 2,6-piridindikarboksilik asit *N*-oksit ($H_2$26pkao) ile Ni(II) {(Ni(26pkao)(bpy)$_{0,5}$(H_2O)).2H_2O} [96], Zn(II) {[Zn_2(26pkao)$_2$(bpy)$_2$(H_2O)$_2$.3H_2O]$_n$} [97], 1,2-bis(4-piridil)etan'ın Ni(II) {{[Ni_2(pdco)$_2$(bpe)(H_2O)$_2$].4H_2O}$_n$} [98], 2,3,5-piridintrikarboksilik asit ($H_3$235ptc) ile Cd(II) {[Cd_3(235ptc)$_2$(bpy)(H_2O)$_4$]} [99] ve 6-metil-2,3,5-piridintrikarboksilik asit (H_3M235ptc) ile Ag(I) {[Ag_4(HM235ptc)$_2$(bpy)$_3$].4.5H_2O} [100], 2,4,6-Piridintrikarboksilik asit (H3ptc) ile Fe(III) {(Hbpy)2[Fe(ptc)(Hptc)].3H_2O} [101], Co(II) {[Co(bpy)(H_2O)$_4$]$_n$[Co(ptc)(H_2O)]$_{2n}$ [102], [Co(ptc)(Hbpy)(H_2O)$_2$].2H_2O [103] ve [Co_2(Hptc)$_2$(bpy)(H_2O)$_4$].2H_2O [104]}, Ni(II) {[Ni(ptc)(bipy).4,5H_2O]} [105], Cu(I)/Cu(II) {[Cu_2(ptc)(bpy)].H_2O}$_n$} [106] ve Zn(II) {[Zn(bpy)(Hptc).bul.H_2O]$_n$ [107], [Zn_2(ptc)$_2$(pby)(H_2O)$_4$].2H_2O} [108], 2,3,5,6-piridintetrakarboksilik asit (H_4ptka) ile Ag(I) {{[Ag_2(H_2ptka)(bpy)$_2$].3H_2O}n} [109], Cu(II) {{[Cu_2(ptka)(bpy)(H_2O)$_2$].3H_2O}$_n$, {[Cu_2(ptka)(bpy)(H_2O)$_2$].2H_2O}$_n$ [110] [Cu_3(H_2O)$_4$(Hptka)$_2$(bpy)$_2$].3H_2O}, Zn(II) {[Zn_4(H_2O)$_6$(ptka)$_2$(bpy)].5H_2O} [111] ve 1,2-bis(4-piridil)etilen (bpe) ile Zn(II) {{[Zn_2(Hptka)$_2$(Hbpe)$_2$].5H_2O}, [Zn_2(ptka)(bpe)$_{1,n}$]$_n$} [110] kompleksleri sentezlenmiş ve yapıları çeşitli spektroskopik metotlar ile karakterize etmişlerdir.

2,2'-bipiridin-3,3',6,6'-piridintetrakarboksilik asit (H_4bptc) ile 1,2-bis(4-piridil)etilen'in Co(II) {[Co_2(H_2bptc)$_2$(H_2O)$_4$].bpe.9H_2O}, Ni(II) {[Ni_2(H_2bptc)$_2$(H_2O)$_4$].bpe.9H_2O} ve 1,4-di(4-piridil)etan ile Ni(II) {[Ni_2(H_2bptc)$_2$(H_2O)$_4$].0,5bpp.7H_2O} [112], 4,4'-bipiridin-2,2',6,6'-piridintetrakarboksilik

asitin (H_4bptca) Co(II) {{[Co(H_2O)$_6$][Co_3(bptca)$_2$(H_2O)$_2$].10H_2O}$_n$}, Ni(II) {[Cu_2(bptca)(H_2O)$_4$]$_n$} [113], La(III), Ce(III), Sm(III), Tb(III), Dy(III), Ho(III) {{[Ln(Hbptca)(H_2O)].3H_2O}$_n$ [Ln = La, Ce, Sm], [Ln_4(bptca)$_3$(H_2O)$_4$]$_n$ [Ln = Tb, Dy, Ho)]} [114] ve 1,3,5-tris(imidazol-1-yilmetil)-2,4,6-trimetilbenzen (titmb) ile Mn(II) {[Mn_4(bptca)$_2$(titmb)(H_2O)$_7$].DMF.4H_2O}, Co(II) {[Co_2(bptca)(titmb)$_2$].13H_2O} ve Ni(II) {[Ni_2(bptca)(titmb)$_2$].13H_2O} [115] kompleksleri sentezlenmiş ve yapıları çeşitli spektroskopik çalışmalar ile karakterize etmişlerdir.

3. SONUÇLAR

Piridinkarboksilik asit ve proton vermiş formları ile birçok çalışma yapılmaktadır. Bu bileşiklerin antioksidan, antifungal, antimikrobiyal, antitümor, antikanser, antiinflamatuar, antiülser, antidiyabetik, antimütajen, süperoksit giderici ve radyoprotektif aktiviteye gibi biyolojik özelliklere sahiptir. Bipiridin türevlerinin antihipertansif, antibakteriyel, anti psikotik, kas gevşetici, analjezik, antioksidan, antidiyabetik, antiinflamatuar, antikanser, antisıtma, enzim inhibisyonu, antidepresan, antikolinerjik gibi biyolojik aktiviteleri mevcuttur. Piridinkarboksilik asit ve bipiridin türevlerinden elde edilecek proton transfer tuzları ve metal kompleksleri de benzer özelikler göstereceği aşikardır. Literatürde yapılan incelemeler sonucunda bu iki grubun bir arada bulunduğu metal komplekslerinin çok, ancak biyolojik özeliklerinin daha az çalışıldığı gözlenmiştir. Bu iki gruptan elde edilecek metal komplekslerinin biyolojik özelliklerin daha ayrıntılı bir şekilde çalışılması literature önemli bir katkı olacaktır. Bu çalışma bu açıklığı belitmek için yapılmıştır.

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