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Formation of Polymeric Assemblies of Six-Coordinate Metal Complexes with Mixed Bridges of Dicarboxylato-Azido

Riyadh M. Ahmed, Taki A. Himdan, Ahmed T. Numan and Mohamad J. Al-Jeboori[١]
Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad,
P.O.Box٤١٥٠, Adhamiya Baghdad-Iraq.
[١]E-mail: mohamadaljeboori@yahoo.com.

Abstract

New polydentate ligand namely bis(N-carboxylatoethyl)-٤,٤`-dipyridinium) L was synthesised from the reaction of ٤,٤`-dipyridine with ethyl chloropropionate. Polymeric complexes of general formulae $[Cr_٢(L)(N_٣)_٤]Cl_٢.H_٢O$, $Na_٢[Ag_٢(L)(N_٣)_٤].H_٢O$ and $[M_٢(L)(N_٣)_٤].nH_٢O$, where (M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II); (where n = ٢;١;١;١;٠;١ and ١, respectively)) are reported. The mode of bonding and overall geometry of the complexes were determined through physico-chemical and spectroscopic methods. These studies revealed octahedral geometry complexes. Molecular structure for the complexes has been optimised by CS Chem ٣D Ultra Molecular Modelling and Analysis Program and supported a six coordinate geometry.

Keywords: Polymeric complexes; Bridged zido-carboxylato ligands; Bis (N-carboxylatoethyl) ٤,٤`-dipyridinium); Structural study, theoretical treatment.

Introduction

Coordination polymers chemistry based on organic-metal framework is an interested hot topic in the synthetic inorganic chemistry, and recently a range of these compounds using different synthetic approaches have been reported [١]. These interested materials shown a range of applications includes light harvesting and magnetic properties. The design and synthesis of magnetic coordination polymers with peculiar structure and potential application have become a focus of intense research activities in the fields of coordination and material chemistry [٢]. The key to designing such material is based on the type of the bridging ligand that can effectively mediate the magnetic interactions and construct novel structures [٣]. Several parameters are influenced the self-assembly of coordination polymers. These include: medium; pH; temperature; the nature of metal ions; coordination geometry; stereochemistry; and number of coordination donors provided by ligands [٤]. Synthesis and fabrication of electro-conductive materials has been a great challenge in coordination polymers [٥]. These polymers show a range of applications and can be used as optoelectronic devices such as electroluminescent devices, thin-film transistors, and solar cells[٦]. Metal complexes with bridging azido moiety have provided unique structures and magnetic properties. Furthermore, the carboxylate group can also efficiently transmit magnetic exchange. Therefore, combining azide and carboxylate moieties in one system is an interesting approach for constructing new materials and modulating magnetic behaviours. The employment of neutral dicarboxylates as ligands and/or combining to ٤,٤`-dipyridine has the potential coordination sites involving both nitrogen of dipyridine and the carboxylate oxygen [٧]. It can coordinate in a variety of coordination modes [٨], and provide several possibilities in creating supramolecular architectures through hydrogen bonds and π- π interactions; it has been widely used to synthesise mononuclear, dinuclear, trinuclear, and coordination polymeric compounds.

Experimental

Materials and Methods

All reagents were obtained commercially (Aldrich) and used without further purification. Solvents used in the synthesis were distilled from appropriate drying agent immediately prior to use.

Physical Measurements

Elemental analyses (C, H and N) were carried out on a Heraeus instrument (Vario EL). IR spectra were recorded as KBr discs using a Shimadzu ٨٤٠٠ S FTIR spectrophotometer from ٤٠٠٠-٤٠٠ cm$^{-١}$. Melting points were obtained on a Electro-thermal Stuart melting point SMP٤٠ capillary melting point apparatus and are uncorrected. Electronic spectra were measured from ٢٠٠-١١٠٠ nm for ١٠$^{-٣}$ M solutions in DMSO at ٢٥°C using a Shimadzu ١٨٠٠ spectrophotometer. ^{١}H- ^{١٣}C-NMR spectra were acquired in DMSO–d$_{٦}$ solution using a Jeol ٤٠٠ MHz spectrometer with tetramethylsilane (TMS) as an internal standard for ^{١}H NMR analysis. Mass spectra for ligand and some metal complexes were obtained by positive Electron-Impact (EI), accurate Electrospray (ES) and Matrix Assisted Laser Desorption Ionisation Time of Flight MS (MALDI-TOF MS) was recorded on a VG autospec micro mass spectrometer on BRUKER DALTONICS. The spectra were recorded at the EPSRC Swansea Mass Spectroscopy Facility, U.K. Metals were determined using a Shimadzu (A.A) ٦٨٠ G atomic absorption spectrophotometer. Chloride content was determined using potentiometer titration method on a ٦٨٦-Titrp processor-٦٦٥Dosimat-Metrohm Swiss. Conductivity measurements were made with DMSO solutions using a PW ٩٥٢٦ digital conductivity meter and room temperature magnetic moments were measured with a magnetic susceptibility balance (Johnson Matthey Catalytic Systems Division).

Synthesis

Preparation of the ligand

The preparation of the ligand was adopted according to a published method [٨] and as follows:

A solution of ethyl chloropropionate (٢,٥١ g, ٢٠ mmol) was added slowly to a mixture of ٤,٤`-bipyridine (٢ g, ١٠ mmol) dissolved in acetone (٢٥ mL). The resulting solution was allowed to reflux for ٧٢ h. After the acetone was removed under reduced pressure a green residue was left, and then a mixture of HCl (٥٠ mL, ٥% w/v) was added. The resulting mixture was heated under reflux for ٢٤ h to give a yellow solution. Removal of solvent afforded a pale yellow powdery product; yield (٢,٢٤ g, ٥٨٪). The product was then dissolved in (٥٠ mL) of water, and silver (I) oxide (١,٥ g, ٠,٠٠٦٥ mmol) was added, with stirring, to remove chloride ions. The white precipitate was filtered off, and the filtrate was then dried to yield a pale yellow solid, which was recrystallised from water/ethanol (١:٤, v/v) to give ligand (L) as a yellow solid; yield (١,٧٠ g, ٤٤٪), m.p. = ٢٤٢ °C. ^{١}H NMR data (ppm), δ_{H}(٤٠٠ MHz, DMSO-d$_{٦}$): shows signals at ٢,٣١-٢,٣٣ (٤H, t, C $_{٢}$, $_{٢`}$-*H*), This signal is shifted to upfield due the attachment to electron withdrawing group, and therefore the (-CH$_{٢}$) group is shielded and appeared at lower chemical shift, ٤,٧١-٤,٧٢ (٤H, t, *J*=٦,٨٠ Hz, C $_{٣}$, $_{٣`}$-*H*), This peak is shifted to downfield due to its attachment to the nitrogen atom, electron withdrawing group, and therefore the (-CH$_{٢}$) group is deshielded and appeared at higher chemical shift, ٨,٦٠-٨,٦٢ (٤H, d, *J*=٧,٣٣, C$_{٥,٥`,٧,٧`}$), ٩,١٢-٩,١٣ (٤H, d, *J* =٦,٨٧, C $_{٤,٤`,٨,٨`}$). ^{١٣}C NMR: shows chemical shift at ٢٩,٩٩ (C$_{٢,٢`}$), ٥٨,٦٩ (C$_{٣,٣`}$), ١٢٤,٩٣ (C$_{٥,٥`,٧,٧`}$), ١٢٥,٢٤(C$_{٥,٥`,٧,٧`}$), ١٤٥,٧٠ (C $_{٤,٤`,٨,٨`}$), ١٥٣,٦٠ (C $_{٦}$, $_{٦`}$), ١٧٧,٠٠ (C $_{١}$, $_{١`}$). The positive ES mass spectrum of the ligand showed the following fragments; ٣٠١ (٥٪) M^{+}, corresponding to $C_{١٦}H_{١٦}N_{٢}O_{٤}$, ٢٥٧ (٣٢ %) [M-CO$_{٢}$]$^{+}$, ٢٢٩ (٦٨٪) [M-(CO$_{٢}$+CH$_{٢}$CH$_{٢}$)]$^{+}$, ١٥٧ (١٠٠٪) [M-(-(CO$_{٢}$+CH$_{٢}$CH$_{٢}$+CH$_{٢}$CH$_{٢}$CO$_{٢}$)]$^{+}$, respectively.

General synthesis of polymeric complexes with ligand

A mixture of metal chloride (٠,٤٩ mmol) (٠,١٣, ٠,٠٩, ٠,٠٩, ٠,١١, ٠,١١, ٠,٠٨, ٠,٠٦, ٠,١١ and ٠,٠٨ g), L (٠,٤٩ mmol) (٠,١٥ g), and NaN$_{٣}$ (٠,٩٩ mmol) (٠,٠٦٤ g) in water/ethanol (٥٠ mL, ٤:٦ v/v) was stirred for ٣٠ min at room temperature, then the mixture was refluxed for ٣٠ min. Slow evaporation of the solution at room temperature yielded green crystals of Cr(III) complex within two weeks, washed with (٥ mL) of diethyl ether, and then dried under vaccu. Yield: (٠,٢٩٧g, ٦٨٪). Elemental analysis data, colours, and yields for the complexes are given in Table (١).

Table (١)
Colours, yields, elemental analyses, and molar conductance values.

Formula	Colour	M.P °C	M.W $gmole^{-١}$	Yield %	Micro analysis found (calc)%				
					C	H	N	Metal	Cl
$C_{١٦}H_{١٨}Cl_{٢}Cr_{٢}N_{١٤}O_{٥}$	Green	Dec ٣٤٦	٦٦١,٣٠	٦٨	٢٧,٨٨ (٢٩,٠٦)	٢,٨١ (٢,٧٤)	٢٨,٢٦ (٢٩,٦٥)	١٤,٦٣ (١٥,٧٣)	١٠,٠٥ (١٠,٧٢)
$C_{١٦}H_{٢٠}Mn_{٢}N_{١٤}O_{٦}$	Pale brown	Dec ٣٢٧	٦١٤,٣٠	٦٩	٣١,١٧ (٣١,٢٨)	٣,١٩ (٣,٢٨)	٣٣,٩١ (٣١,٩٢)	١٨,٩١ (١٧.٨٩)	٠,٦١
$C_{١٦}H_{١٨}Fe_{٢}N_{١٤}O_{٥}$	Brown	Dec ٢٠٦	٥٩٨,١٠	٨٨	٣١,٣٦ (٣٢,١٣)	٢,٨٤ (٣,٠٣)	٣٣,٨٠ (٣٢,٧٩)	١٨,٩٨ (١٨,٦٧)	١,٤٠
$C_{١٦}H_{١٨}Co_{٢}N_{١٤}O_{٥}$	Blue	Dec ٣٢٩	٦٠٤,٢٧	٦٨	-	-	-	١٨,٧٣ (١٩,٥١)	٠,٧٠
$C_{١٦}H_{١٨}Ni_{٢}N_{١٤}O_{٥}$	Green	Dec ٣٢٢	٦٠٣,٧٩	٧٦	٣٠,٨١ (٣١,٨٣)	٢,٩٥ (٣,٠٠)	٣٣,٤٨ (٣٢,٤٨)	١٩,٥٤ (١٩,٤٤)	١,٠٢
$C_{١٦}H_{١٦}Cu_{٢}N_{١٤}O_{٤}$	Green	Dec ٣٢٥	٥٩٥,٤٨	٧٤	٣٢,٦٥ (٣٢,٢٧)	٢,٥٦ (٢,٧١)	٣٢,٩٣ (٣٢,٩٣)	٢١,٠٣ (٢١,٣٤)	١,١٥
$C_{١٦}H_{١٨}Zn_{٢}N_{١٤}O_{٥}$	pale yellow	Dec ٣٠٣	٦١٧,١٩	٧٨	-	-	-	٢١,١٧ (٢١,١٩)	٠,٣٢
$C_{١٦}H_{١٨}Cd_{٢}N_{١٤}O_{٥}$	White	Dec ٣١٩	٧١١,٢٣	٦٨	-	-	-	٣٠,٧٦ (٣١,٦١)	٠,٤٢
$C_{١٦}H_{١٨}Na_{٢}Ag_{٢}N_{١٤}O_{٥}$	White	١٨٣	٧٤٨,١٢	٦٣	-	-	-	٢٧,٨٢ (٢٨,٨٤)	٠,٤٣

(calc) = calculated; Dec = decomposed.

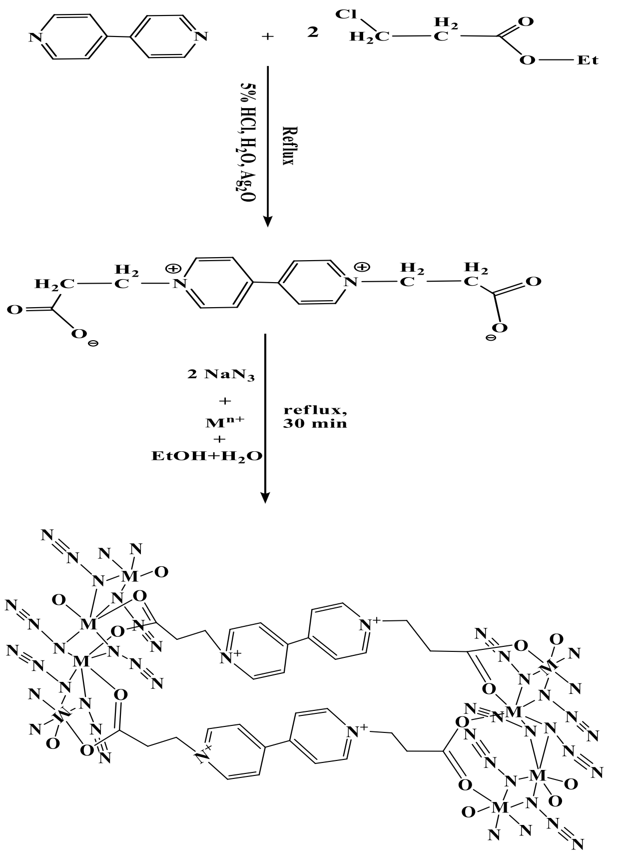
Molecular modelling

٣D molecular modelling of the proposed structure of the complexes was performed using CS Chem ٣D Ultra Molecular Modelling and Analysis Program [٩]. It is an interactive graphics program that allows rapid structure building, geometry optimization with minimum energy and molecular display. It is well known program and has the ability to handle transition metal complexes [١٠]. The correct stereochemistry was assured through the manipulation and modification of the molecular coordinates to obtain reasonable low energy molecular geometries.

Results and Discussion

Chemistry

The reaction of ٤,٤`-dipyridine with ethyl chloropropionate in mole ratio of ١:٢ gave the multidentate carboxylate ligands bis(N-carboxylatoethyl)-٤,٤`-dipyridinium) L, in moderate yield (Scheme ١). The ligand was characterised by elemental analysis (Table (١)), IR (Table ٢), UV–Vis (Table (٣)) spectroscopy. The neutral and di-electrolyte complexes of the general formula $[Cr_{٢}(L)(N_{٣})_{٤}]Cl_{٢}.H_{٢}O$, $Na_{٢}[Ag_{٢}(L)(N_{٣})_{٤}].H_{٢}O$ and $[M_{٢}(L)(N_{٣})_{٤}].nH_{٢}O$ (where M = Mn, Fe, Co, Ni, Cu, Zn and Cd, n= ٠,١,٢); were obtained (Scheme (١)). The complexes are air-stable solids, soluble only in DMSO, and not soluble in other common organic solvents. The coordination geometries of the complexes were deduced from their spectra. The analytical data Table (١) agree well with the suggested formula. Conductivity measurements of the Cr(III) and Ag(I) mixed complexes lie in the ٧١,٤١ and ٧٨,٤٦ $cm^{٢}\Omega^{-١}$ $mol^{-١}$ range, indicating their ١:٢ electrolytic behaviour, but non-electrolyte for other complexes [١١] Table (١).



Where M= Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, and Ag^{I}.

Scheme (١) Synthesis route of ligand and the proposed polymeric complexes.

NMR and IR Spectra

The NMR spectra of the ligand were consistent with the proposed structural formulae (see Experimental section). ^{١}H NMR spectrum of the ligad (Figure ١) shows signals at ٢,٣١-٢,٣٣ (٤H, t, C ٢, ٢`-*H*). This signal is appeared at up field due the attachment to electron withdrawing group, and therefore the (-$CH_{٢}$) group is shielded and appeared at lower chemical shift. Chemical shift equivalent to ٤ protons at ٤,٧١-٤,٧٢ assigned to C ٣, ٣`-*H*. This peak is shifted to downfield due to its attachment to the nitrogen atom, electron withdrawing group, and therefore the (-$CH_{٢}$) group is deshielded and appeared at higher chemical shift. The important infrared bands for the ligands and their complexes together with their assignments are listed in Table (٢). The IR spectrum of the ligand shows characteristic bands at ١٦٣٢ and ١٤٥٨ assigned for ν_{as}(COO) and ν_{s}(COO), respectively [٢٣]. Bands at ١٥٩٧ and ١٥٧٨ cm$^{-١}$ are due to the ν(C=N) and ν(C=C) [٢٤], respectively. The IR spectra of the complexes exhibited ligand bands with the appropriate shifts and the M-O and M-N frequencies due to complex formation Table (٢). The IR spectra of the polymeric complexes display the ν_{as}(COO) stretching bands around ١٦٠١-١٦٢٨ cm$^{-١}$ and ν_{s}(COO) stretching bands around ١٤٠٠-١٤٦٢ cm$^{-١}$, respectively. These bands were shifted to lower frequency compared with that in the free ligand, except for Ag(I) which shifted to higher frequency.

This can be attributed to delocalisation of metal electron density ($t_{٢g}$) to the π-system of the ligand [١٢]. The difference between ν_{as}(COO) and ν_{s}(COO) is characteristic for a bidentate coordination mode in which the carboxylato moiety adopts the *syn*-*syn* orientation except Ag (I) complex the carboxylato moiety adopts *syn*-*ant*i mode [١٣]. The strong new bands located at ٢٠٤١-٢١١٤ cm$^{-١}$ and ١٣٢٩-١٣٦٩ cm$^{-١}$ were attributed to ν_{as}($N_{٣}$) and ν_{s}($N_{٣}$), respectively [١٤]. The six coordination is referred to the coordination of four azide group as N(μ١,١) fashion and the oxygen of carboxylate moieties to the metal atoms [١٥]. At lower frequency the complexes exhibited bands around ٤٠٦-٤٨٦ cm$^{-١}$ may be assigned to ν(M-N), while the band at ٤٩٨-٥٨٣ cm$^{-١}$ can be assigned to ν(M-O) for the complexes [١٦]. The appearance of ν(M–O) at frequency higher than that of ν(M–N) due to the larger dipole moment change for M–O compared to M–N, the ν(M–O) usually appears at higher frequency than the ν(M–N) band [١٧].

Table (٢)
IR frequencies (cm⁻١) of the compounds.

Complex	ν O-H	νCH$_2$	ν$_{as}$N$_3$	ν$_{as}$COO	νC=N	ν$_s$COO	δO-H	ν$_s$N$_3$	νC-N	νM-O	νM-N	Δ(ν$_{as}$-ν$_s$)
L	-	2851	-	1632	1597	1458	-	-	1218	-		174
$[Cr_2(L)(N_3)_4]Cl_2.H_2O$	3414	2862	2114 2068	1620	1595	1420	1555	1335	1223	536 562	424 440	200
$[Mn_2(L)(N_3)_4].2H_2O$	3387	2909	2066	1609	1572	1418	1522	1333	1223	505 561	419 434	191
$[Fe_2(L)(N_3)_4].H_2O$	3439	2841	2064	1617	1610	1400	1560	1346	1213	536 563	406 436	217
$[Co_2(L)(N_3)_4].H_2O$	3404	2914	2079	1607	1570	1416	1533	1342	1221	546 565	419 457	191
$[Ni_2(L)(N_3)_4].H_2O$	3402	2889	2091 2060	1605	1636	1416	1522	1344	1225	498 563	432	189
$[Cu_2(L^3)(N_3)_4]$	3422	2828	2041	1628	1593	1412	1485	1369	1223	501 532 574	440 474	216
$[Zn_2(L)(N_3)_4].H_2O$	3416	2846	2085	1611	1533	1416	1491	1344	1219	536 567	422 486	195
$[Cd_2(L)(N_3)_4].H_2O$	3418	2833	2060	1601	1638	1418	1537	1329	1221	500 565	444 463	183
$Na_2[Ag_2(L)(N_3)_4].H_2O$	3449	2824	2045	1628	1593	1462	1482	1361	1227	501 583	478 483	166

Mass Spectra

The mass spectrum of the ligand was consistent with the proposed structural formulae (see Experimental section). The positive ion MALDI mass spectra for several complexes were reported. The mass spectrum of $[Co_{٢}(L)(N_{٣})_{٤}].H_{٢}O$ showed several peaks corresponding to successive fragmentation of the molecule. The complex showed peak at m/z ٦٠٤,٨٦ (٧٪) $(M)^+$ represents the molecular ion peak of the complex. Other distinct peaks were observed in the mass spectrum at m/z ٤٤٤,٧٣ (٥٪), ٤١٨,٧٢ (١٠٪), ٣٥٢,٦٤ (٥٦٪), ٣٣٦,٦٥ (١٠٠٪), ٢٨٤,٦٠ (٥٪) and ٢٠٢,٥٦ (٣٪) can be assigned to the $(M-(٢N_{٢}+٢CO+CH_{٤}+N_{٢}H_{٤}))^+$, $(M-(٢N_{٢}+٢CO+CH_{٤}+N_{٢}H_{٤}+CN)^+$, $(M-(٢N_{٢}+٢CO+CH_{٤}+N_{٢}H_{٤}+٢CN+C_{٣}H_{٤})^+$ and $(M-(٢N_{٢}+٢CO+CH_{٤}+N_{٢}H_{٤}+٢CN+C_{٣}H_{٤}O)^+$, $(M-(٢N_{٢}+٢CO+CH_{٤}+N_{٢}H_{٤}+٢CN+C_{٣}H_{٤}O+C_{٢}H_{٢}+CN)^+$, $(M-(٢N_{٢}+٢CO+CH_{٤}+N_{٢}H_{٤}+٢CN+C_{٣}H_{٤}O+C_{٢}H_{٢}+CN+N_{٤}+CN)^+$ fragments, respectively. The spectrum of $[Zn_{٢}(L)(N_{٣})_{٤}].H_{٢}O$, displayed peak at m/z = ٦١٧,٥٣ $(M)^+$ (٧٪) represents the molecular ion peak of the complex. Other distinct peaks were observed in the mass spectrum at m/z ٥٤٥,٤٢ (٣ %), ٤٠٥,٠٠ (٦ %), ٣٣٢,٩٨ (٨ %), ٢٢٩,٠٩ (٢٤ %), ١٨٨,١٨ (٤٧٪) and ١٥٧,١٨ (١٠٠٪) can be assigned to the $(M-(N_{٢}+N_{٢}O))^+$, $(M-(٣N_{٢}+CO+CH_{٢}CH_{٢})^+$, $(M-(CH_{٢}CH_{٢}+CO_{٢})^+$ and $(M-(٢CN+٢CH=CH))^+$, $(M-(٢CN+٢CH=CH+C_{٣}H_{٥}))^+$ and $(M-(٢CN+٢CH=CH+C_{٣}H_{٥}+N\text{-}OH))^+$ fragments, respectively. These results are similar to those of analogous complexes reported earlier by others [١٨].

Electronic spectra and magnetic moment measurements

The UV-Vis spectrum of L (Fig.(٢)) exhibits a high intense absorption peak at ٢٧٩ nm, assigned to the overlapping peaks of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ [١٩]. The electronic spectrum of the Cr(III) complex shows a high intense peaks at ٢٦٣ nm due to intra-ligand. The low intense peaks at ٧٥٦ and ٤٦٧ nm were attributed to the $^{٤}A_{٢}g \rightarrow {}^{٤}T_{٢}g^{(F)}$ ($\nu_{١}$) and $^{٤}A_{٢}g \rightarrow {}^{٤}T_{١}g^{(F)}$ ($\nu_{٢}$) transitions, respectively. These bands attributed to the spin allowed d-d transitions, indicating an octahedral geometry around the Cr(III) atom [٢٠]. The electronic spectrum of the Mn(II) complex shows three peaks at ٢٦٨ nm due to intra-ligand, ٣٦٢ nm due to charge transfer and ٦٤٣ nm assigned to $^{٦}A_{١}g \rightarrow {}^{٤}T_{١}g^{(G)}$ transition [٢١]. Electronic data of other complexes displayed peaks confirming octahedral geometries around metal atoms Table (٣). The $d^{١٠}$ complexes exhibited bands at ٢٦٦, ٢٦٥ and ٢٦٤ nm, respectively which assigned to the ligand field for Zn(II), Cd(II) and Ag(I) complexes, respectively. The room temperature magnetic moments of the complexes are reported in Table (٣). Complexes show magnetic moments in the range ٠,٧٩–٣,٠٣ BM. The very low observed moments are allowed us to conclude safely that the complexes are antiferromagnetic [٢٢].

Table (٣)
Magnetic moment, u.v-vis spectral data in DMSO solutions and total minimisation energy.

Compound	***μ_{eff} BM per atom***	***Band Position λ_{nm}***	***Wave number (cm$^{-١}$)***	***Extinction coefficient ε_{max} (dm^{٣} mol$^{-١}$ cm$^{-١}$)***	***Assignment***	***Total energy Kcal/mol***
L	-	٢٧٩	٣٥٨٤٢	٢٠٤٦	n $\rightarrow\pi^*$and $\pi^*\rightarrow\pi^*$	-١٣٨,١١٥٤
$[Cr_{٢}(L)(N_{٣})_{٤}]Cl_{٢}.H_{٢}O$	٢,٤٤	٢٦٣ ٤٦٧ ٧٥٦	٣٨٠٢٣ ٢١٤١٣ ١٣٢٢٨	١٧٨٥ ٤ ١	Intra-ligand $^{٤}A_{٢}g \rightarrow {}^{٤}T_{٢}g\ (\nu_{١})$ $^{٤}A_{٢}g^{(F)} \rightarrow {}^{٤}T_{١}g\ (\nu_{٢})$	١٤٨,٨٩٥٠
$[Mn_{٢}(L)(N_{٣})_{٤}].٢H_{٢}O$	٣,٠٣	٢٦٨ ٣٦٢ ٦٤٣	٣٧٣١٣ ٢٧٦٢٤ ١٥٥٥٢	٢١٥٠ ٢١ ١	Intra-ligand C.T $^{٦}A_{١}g \rightarrow {}^{٤}T_{١}g^{(G)}$	١٤٩,٣٧٧٦
$[Fe_{٢}(L)(N_{٣})_{٤}].H_{٢}O$	٠,٧٩	٢٧٢ ٣٦٢ ٥٨٦	٣٦٧٦٤ ٢٧٦٢٤ ١٧٠٦٥	٢١٤٤ ٢٠٦ ٢١	L.F C.T $^{٥}T_{٢}g \rightarrow {}^{٥}Eg$	١٢٨,٣٢٦٢
$[Co_{٢}(L)(N_{٣})_{٤}].H_{٢}O$	١,٧٧	٢٧٠ ٣٤٦ ٦٣٣ ٦٧٧	٣٧٠٣٧ ٢٨٩٠١ ١٥٧٩٨ ١٤٧٧١	٢٠٣٦ ١٢٩ ٦١ ٧٣	L.F C.T $^{٤}T_{١}g^{(F)} \rightarrow {}^{٤}A_{٢}g^{(F)}$ $^{٤}T_{١}g^{(F)} \rightarrow {}^{٤}A_{٢}g^{(F)}$	٢٠٧,٥٥١٤
$[Ni_{٢}(L)(N_{٣})_{٤}].H_{٢}O$	١,٥٥	٢٦٦ ٣٠٣ ٦٣٣	٣٧٥٩٤ ٣٣٠٠٣ ١٥٧٩٨	٧٥٨ ١٢٤ ٥٣	L.F C.T $^{٣}T_{٢}g \rightarrow {}^{٣}T_{١}g^{(F)}$	٦٤٩,٥٤٦٥
$[Cu_{٢}(L)(N_{٣})_{٤}]$	١,٠٨	٢٦٨ ٦١١	٣٧٣١٣ ١٦٣٦٧	١٣٥٠ ٥٠	L.F $^{٢}B_{١}g \rightarrow {}^{٢}B_{٢}g$	١٥٠,٠٤٩٣
$[Zn_{٢}(L)(N_{٣})_{٤}].H_{٢}O$	-	٢٦٦	٣٧٥٩٤	١٤٤٣	L.F	١٣٢,٢٩٦٥
$[Cd_{٢}(L)(N_{٣})_{٤}].H_{٢}O$	-	٢٦٥	٣٧٧٣٦	٧٢٣	L.F	١٥٩,٩٧٣٩
$Na_{٢}[Ag_{٢}(L)(N_{٣})_{٤}].H_{٢}O$	-	٢٦٤	٣٧٨٧٩	٩٣٥٠	L.F	١٣٠,٠٠١٢

٣D molecular modelling and analysis of bonding modes

Molecular mechanics attempts to reproduce molecular geometries, energies and other features by adjusting bond length, bond angles and torsion angles to equilibrium values that are dependent on the hybridization of an atom and its bonding scheme. In order to obtain estimates of structural details of these complexes and in view the six-coordination of all the complexes, we have optimised the molecular structure of the ligands and their M-complexes and we have included $[Ni_{٢}(L)(N_{٣})_{٤}].H_{٢}O$ as a representative compound. The detail of bond lengths and bond angles per the ٣D molecular structure is given in Table ٤. Energy minimization was repeated several times to find the global minimum [٢٣١]. The energy minimization value for octahedral and without restricting the structure for the prepared M-compounds are presented in Table (٤). The molecular modelling for the modulated Ni(II)-complex (Fig. (٦) and Table (٤)) shows the bond lengths bond angles around Ni atom, indicating a distorted octahedral geometry around Ni(II) ion [٢٤], and thus the proposed structure of the Ni(II)-complexes are acceptable.

Table (٤)
The calculated bond length and bond angle of $[Ni_{٢}(L^{٣})(N_{٣})_{٤}].H_{٢}O$.

Type of Bond	*Bond length (A°)*	*Type of Bond*	*Bond angle(°)*
$Ni_{١}$-$N_{١}$	١,٨٢٦	$O_{١}$- $Ni_{١}$-$N_{١}$	١٨٠,٠٠
$Ni_{١}$-$N_{٣}$	١,٨٢٦	$O_{١}$- $Ni_{١}$-$N_{٢}$	٨٩,٩٩٣
$Ni_{١}$-$N_{٤}$	١,٨٣٨	$O_{١}$- $Ni_{١}$-$O_{٢}$	٨٩,٩٩٧
$Ni_{١}$-$N_{٢}$	١,٨٢٦	$N_{١}$- $Ni_{١}$-$O_{٢}$	٩٠,٠٠٤
$Ni_{١}$-$O_{٢}$	١,٧٩٠	$N_{٣}$- $Ni_{١}$-$O_{٢}$	٧٤,١٠٣
$C_{١}$-$O_{١}$	١,٤٠٢	$N_{٤}$- $Ni_{١}$-$N_{٢}$	٦٤,٦٠٧
$N_{٣}$-$N_{٥}$	١,٣٥١	$N_{٤}$- $Ni_{١}$-$O_{٢}$	١٦٣,٧٣٧
$N_{٤}$-$N_{٦}$	١,٣٥١	$Ni_{١}$-$N_{٣}$-$Ni_{٢}$	٩٠.٠٠
		$Ni_{١}$-$N_{٤}$-$Ni_{٢}$	٨٩,٦٤٢

Conclusion

In this paper, we have explored the synthesis and coordination chemistry of some carboxylato-azido metal-complexes derived from the polydentate ligand L. The ligand behaves as a neutral species upon complexation with the involvement of the nitrogen atoms of the azido groups in coordination for all complexes. The magnetic susceptibilities and electronic spectra of the complexes indicated that they are antiferrromagnetic with octahedral geometry about metal atoms.

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الخلاصة

تضمن البحث تحضير ليكاند جديد متعدد السن bis(N-carboxylatomethyl)-٤،٤`-dipyridinium من تفاعل ٤-٤-ثنائي بيريدين مع اثيل كلورو بروبيونت. حضرت مونميرات المعقدات لهذه الليكاندات، ذات الصيغة العامة $[Cr_٢III(L)(N_٣)_٤]Cl_٢.H_٢O$، $Na_٢[Ag_٢(I)(L)(N_٣)_٤]H_٢O$ و $[M_٢(L)(N_٣)_٤].nH_٢O$ حيث (M = Mn(II), (II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) .Fe; n = ١،١, ٠،١،١،١،٢) طبيعة الارتباط والاشكال الهندسية لهذه المعقدات شخصت بواسطة طيف الاشعة تحت الحمراء، طيف الاشعة فوق البنفسجية- المرئية، الرنين النووي المغناطيسي، طيف الكتلة، قياسات الحساسية المغناطيسية، التحليل الدقيق للعناصر، لامتصاص الذري، محتوى الكلور و التوصيلية المولارية. اظهرت الدراسات شكل ثماني السطوح حول المراكز الفلزية للمعقدات ويحصل الارتباط من خلال مجاميع الازايد والكاربوكسيلات. التراكيب الجزيئية للمعقدات قد حددت بواسطة CS Chem ٣D Ultra Molecular Modelling and Analysis Program والتي دعمت الشكل سداسي التناسق.