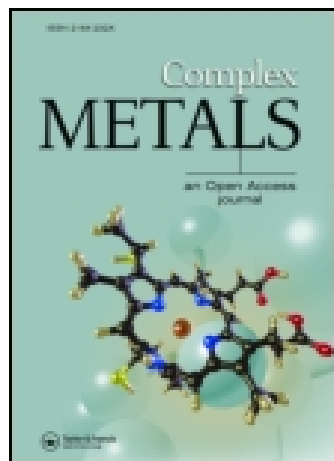


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Formation of polymeric assemblies of six-coordinate metal complexes with mixed bridges of dicarboxylato-azido moieties

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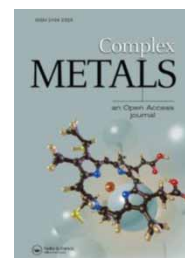
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Article

Formation of polymeric assemblies of six-coordinate metal complexes with mixed bridges of dicarboxylato-azido moieties

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New biscarboxylato zwitterionic ligands, namely bis(N-carboxylatoethyl)-4,4'-dipyridinium) L¹ and bis(N-carboxylatopropyl)-4,4'-dipyridinium) L², were synthesized from the reaction of 4,4'-dipyridine with 3-bromopropanoic acid and 4-bromobutanoic acid, respectively. The reaction of these ligands and the azido coligand with some metal ions resulted in the formation of polymeric complexes of general formulae [Cr₂(Lⁿ)(N₃)₄]Cl₂·H₂O and [M₂(Lⁿ)(N₃)₄] xH₂O, where (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II); n = 1, 2; x = 1, 1, 1, 1, 0, 1, and 1, respectively.) The oxygens of the carboxylato group are coordinated to the metal ion in a bidentate fashion. The mode of bonding and overall geometry of the complexes were determined through IR, UV–VIS, NMR and mass spectral studies, magnetic moment measurements, elemental analysis, metal content, chloride content and conductance. These studies revealed the formation of polymeric assemblies of six-coordinate complexes with distorted octahedral geometries about metal centers.

Keywords: Polymeric complexes; Zwitterionic polydentate ligands; Bis(N-carboxylatoethyl)4,4'-dipyridinium); Bis(N-carboxylatopropyl)-4,4'-dipyridinium); Structural study

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1. Introduction

Coordination polymers chemistry based on the organic-metal framework is an interesting hot topic in the synthetic inorganic chemistry, and recently a range of these compounds using different synthetic approaches have been reported [1]. These interesting materials have shown a range of applications, including light harvesting and magnetic properties. The design and synthesis of magnetic coordination polymers with a peculiar structure and potential application have become a focus of intense research

activities in the fields of coordination and material chemistry [2]. The key to design such materials is based on the type of the bridging ligand that can effectively mediate the magnetic interactions and construct novel structures [3]. Several parameters influenced the self-assembly of coordination polymers. These include: medium; pH; temperature; the nature of metal ions; coordination geometry; stereochemistry and the number of coordination sites provided by ligands [4]. Synthesis and fabrication of electro-conductive materials have been a great challenge in coordination polymers [5]. These polymers show a

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range of applications and can be used as optoelectronic devices such as electroluminescent devices, thin-film transistors and solar cells [6]. Furthermore, bridging ligands such as the carboxylate group can also efficiently transmit magnetic exchange. Therefore, the use of a carboxylate moiety is an interesting approach for constructing new materials and modulating magnetic behaviors. The employment of neutral dicarboxylates as ligands and/or combining with 4,4'-dipyridine has the potential of coordination sites involving both nitrogen of dipyridine and the carboxylate oxygen [7]. It can coordinate in a variety of coordination modes [8], and provide several possibilities in creating supramolecular architectures through hydrogen bonds and π - π interactions; it has been widely used to synthesis mononuclear, dinuclear, trinuclear and coordination polymeric compounds. On the other hand, azide species is widely used in the coordination chemistry. The azide moiety can link metal ions in different fashions, including a bridging mode. Depending on the coordination mode, complexes with particular structures and magnetic properties of the azido species are reported [9,10]. Magnetic exchange mediated via an azido bridge depending on the bridging mode and bonding parameters is well documented. The structures and thus the magnetic properties of metal azido systems are sensitive to the coligands employed in the system. The design of self-assembled polymeric species containing mixed azido and carboxylato bridges are an interesting area of research [11,12]. In this paper, we report the synthesis and spectral investigation of two biscarboxylato ligands, bis(N-carboxylatoethyl)-4, 4-dipyridinium) L^1 and bis(N-carboxylatopropyl)-4, 4-dipyridinium) L^2 and their role with the azido species for the formation of polymeric assemblies with some metal ions.

2. Experimental

2.1. 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.

2.2. Physical measurements

Elemental analyses (C, H and N) were carried out on a Heraeus instrument (Vario EL). IR spectra were recorded as KBr disks using a Shimadzu 8400 S FTIR spectrophotometer from 4000 to 400 cm^{-1} . Electronic spectra were measured from 200 to 1100 nm for 10^{-3} M solutions in dimethyl sulfoxide (DMSO) at 25°C using a Shimadzu 1800 spectrophotometer. Mass spectra for ligands and

some metal complexes were obtained by a positive Electro spray (ES) mass using a Thermo LTQ Orbitrap XL spectrometer. ^1H - ^{13}C -NMR spectra were acquired in a DMSO- d_6 solution using a Jeol 400 MHz spectrometer with tetramethylsilane as an internal standard for ^1H NMR analysis. Melting points were obtained on an Electro-thermal Stuart melting point SMP40 capillary melting point apparatus and are uncorrected. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Chloride content was determined by using the potentiometer titration method on a 686-Titrip processor-665Dosimat-Metrohm Swiss. Conductivity measurements were made with DMSO solution using a PW 9526 digital conductivity meter, and room temperature magnetic moments were measured with a magnetic susceptibility balance (Johnson Matthey Catalytic Systems Division).

3. Synthesis

3.1. Preparation of L^1

The ligand was prepared by adopting a conventional method reported in [13] and as follows:

3.1.1. Synthesis of $\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{NCH}_2\text{CH}_2\text{CO}_2\cdot$

3H₂O (1). 3-Bromopropanoic acid (1.40 g, 0.91 mmol) was stirred with 4,4'-bipyridine (1.42 g, 0.91 mmol) in CH_2Cl_2 (15 mL) for two days. The resulting precipitate was filtered, washed with CH_2Cl_2 (2×5 mL) and dried in a vacuo. The precipitate was recharged in CH_2Cl_2 (20 mL) and stirred with triethylamine (5 mL) for 10 h. The precipitate was filtered, washed with CH_2Cl_2 (2×5 mL) and dried in a vacuo to yield a yellow powder, which was redissolved in water (5 mL) and allowed to slow evaporation at room temperature (RT) to give the title compound. Yield: 57%.

3.1.2. Synthesis of $[(\text{C}_6\text{H}_4\text{NCH}_2\text{CH}_2\text{CO}_2)_2\text{H}]\text{Br}\cdot$

2H₂O(2). 3-Bromopropanoic acid (0.18 g, 0.11 mmol) was added to a mixture of **1** (0.25 g, 0.11 mmol) in CH_2Cl_2 (15 mL). The mixture was allowed to stir at 30°C for five days. The resulting precipitate was filtered, washed with CH_2Cl_2 (3×5 mL) and dried in a vacuo to yield a white powder. The powder was dissolved in water (5 mL) and evaporated at RT to give the title compound. Yield: 0.24 g (73%), m.p. = 242-244°C. Nuclear magnetic resonance (NMR) data (ppm), δ_H (400 MHz, DMSO- d_6): 2.31-2.33 (4H, t, $\text{C}_{2,2'}\text{-H}$), 4.71-4.72 (4H, t, $J = 6.80$ Hz, $\text{C}_{3,3'}\text{-H}$), 8.60-8.62 (4H, d, $J = 7.33$ Hz, $\text{C}_{5,5',7,7'}$), 9.12-9.13 (4H, d, $J = 6.87$ Hz, $\text{C}_{4,4',8,8'}$). δ_C (100.63 MHz, DMSO- d_6): 29.99 ($\text{C}_{2,2'}$), 58.69 ($\text{C}_{3,3'}$), 124.93 ($\text{C}_{5,5',7,7'}$),

145.70 (C_{4,4',8,8'}), 153.60 (C_{6,6'}) and 177.00 (C_{1,1'}). ESI-MS: The positive ES mass spectrum of the ligand showed the following fragments: 301 (5%) [M-Br]⁺ corresponding to C₁₆H₁₆N₂O₄, 257 (32%) [M-CO₂]⁺, 229 (68%) [M-(CO₂ + CH₂CH₂)]⁺ and 157 (100%) [M-(-(CO₂ + CH₂CH₂ + CH₂CH₂CO₂)]⁺.

3.2. Preparation of L²

The method used was analogous to that procedure given for L¹, but with 4-bromobutanoic acid (2.14 g, 2 mmol) in place of 3-bromopropanoic acid. The quantities of the other reagents were adjusted accordingly, and an identical work-up gave L² as a dark yellow solid. Yield: 1.43 g (68%), m.p. 266–268°C. NMR data (ppm), δ_H (400 MHz, DMSO-d₆): 2.16–2.23 (4H, t, J_{HH} = 7.33 Hz, C_{3,3--H}), 2.36–2.49 (4H, t, J_{HH} = 7.33 Hz, C_{2,2--H}), 4.68–4.72 (4H, t, J_{HH} = 14.4 Hz, C_{4,4--H}), 8.65–8.67 (4H, d, J_{HH} = 6.41 Hz, C_{6,6--8,8--H}), 9.28–9.30 (4H, d, J_{HH} = 6.87 Hz, C_{5,5--9,9--H}); δ_C (100.63 MHz, DMSO-d₆): 26.08 (C_{3,3-}), 30.23 (C_{2,2-}), 59.77 (C_{4,4-}), 125.69 (C_{6,6--8,8-}), 145.93 (C_{5,5--9,9-}), 152.17 (C_{7,7-}), 173.38 (C=O). The ES MS (+) mass spectrum of L² showed ion peak at m/z 328.7 (M-Br)⁺ (13%). The other peaks detected at m/z = 284.5 (5%), 242.4 (3%), 198.2 (5%), 156 (100%) and 128 (8%) correspond to [M-CO₂]⁺, [M-(CO₂ + (CH₂)₃)]⁺, [M-(CO₂ + (CH₂)₃ + CO₂)]⁺, [M-(CO₂ + (CH₂)₃ + CO₂ + (CH₂)₃)]⁺ and [M-(CO₂ + (CH₂)₃ + CO₂ + (CH₂)₃ + N₂)]⁺, respectively.

3.3. General synthesis of polymeric complexes with L¹ and L² ligands

A solution of the appropriate ligand (1 mmol) and triethylamine (3 mmol) in water (20 mL) was allowed to stir for 30 min, and then an aqueous solution (10 mL) of NaN₃ (2 mmol) was added. The mixture was allowed to stir for 10 min, and then a solution of metal chloride (1 mmol) in H₂O (5 mL) was added dropwise. The reaction mixture was allowed to stir for 30 min at RT, and then the mixture was refluxed for 1 h, and filtered. The filtrate was concentrated to half of its original volume and acetone (10 mL) was added to afford a precipitate that was filtered and washed with acetone (2 × 5 mL). The solid was dissolved in water (15 mL) and allowed for slow evaporation at RT to yield the title compound. Elemental analysis data, colors and yields for the complexes are given in Table 1.

NMR data (ppm): [Cd^{II}(L²)(N₃)₄]; the ¹H and ¹³C spectra of the complex; δ_H (400 MHz, DMSO-d₆): 2.15–2.22 (4H, C_{3,3--H}), 2.35–2.38 (4H, t, J_{HH} = 14.4 Hz, C_{2,2--H}), 4.65–4.68 (4H, t, J_{HH} = 14.4 Hz, C_{4,4--H}), 8.72–8.75 (4H, t, J_{HH} = 12.0 Hz, C_{6,6--8,8--H}), 9.22–9.24

(4H, d, J_{HH} = 7.2 Hz, C_{5,5--9,9--H}); δ_C (100.63 MHz, DMSO-d₆): 29.34 (C_{3,3-}), 33.99 (C_{2,2-}) and 65.52 (C_{4,4-}), 129.99 (C_{6,6--8,8-}), 150.57 (C_{5,5--9,9-}), 156.05 (C_{7,7-}) and 178.11 (C=O).

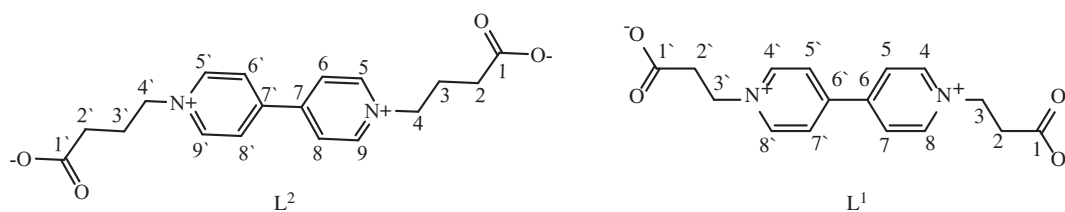
4. Results and discussion

4.1. Chemistry

The new biscarboxylato ligands L¹ and L² were obtained in good yields by the reaction of 4,4'-dipyridine with 3-bromopropanoic acid and 4-bromobutanoic acid, respectively (Scheme 1). The ligands were prepared in two steps in the CH₂Cl₂ medium. The ligands were characterized by elemental analysis (Table 1), IR (Table 2), UV–VIS (Table 3), mass and ¹H, ¹³C-NMR spectroscopy. Polymeric assemblies of the ligands with Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were obtained by heating 1 mmol of each ligand and 2 mmol of azido coligand with 1 mmol of metal chloride, using water. The aim of this work is to obtain complexes in which the carboxylato and azido bridges play a key role in the formation of polymeric assemblies. All attempts to isolate crystals that are suitable for X-ray single crystal diffraction analysis were unsuccessful. Therefore, the ligands and some metal complexes were analyzed by XRD powder diffraction analysis. The XRD patterns for the ligands and their complexes showed the preparation of crystalline materials with the appropriate absorption peaks (see supporting information, Figures SI 1–4). Neutral and di-electrolyte polymeric complexes of the general formulae [M₂(Lⁿ)(N₃)₄·xH₂O (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II); n = 1 or 2; x = 1, 2) and [Cr₂(Lⁿ)(N₃)₄]Cl₂·H₂O were obtained (Scheme 2). It is well documented that the six-coordinate number is one of the most commonly observed coordination number for transition metals. There are several factors that may determine the formation of this coordination number. These include: (1) the size and oxidation state of central ion and (2) the electronic and steric interaction that occurred between ligands upon complex formation. Based on these facts, the prepared complexes adopt their preference for distorted octahedral geometries around metal atoms. The complexes are air-stable solids, soluble only in hot DMSO with stirring, and not soluble in other common organic solvents. The coordination geometries of the complexes were deduced from their spectra. The analytical data (Table 1) agree well with the suggested formulae. The most important infrared bands of the ligands and their complexes together with their assignments are collected in Table 2. The electronic spectra for the ligands and their complexes are presented in Table 3.

Table 1. Colors, yields, elemental analyses and molar conductance values.

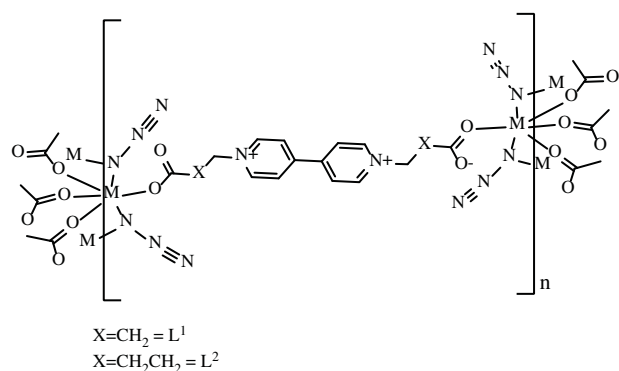
Compound	Color	Yield (%)	m.p.	Found (Calcd) (%)					$\Delta_M(\text{cm}^2\Omega^{-1}\text{M}^{-1})$
				M	C	H	N	Cl	
L ¹	Pale yellow	73	242–244	–	63.97 (63.99)	5.36 (5.37)	9.31 (9.33)	–	–
[Cr ₂ (L ¹)(N ₃) ₄]Cl ₂ ·H ₂ O	Green	66	346 ^a	14.63 (15.73)	27.88 (29.06)	2.81 (2.74)	28.26 (29.65)	10.05 (10.72)	78.46
[Mn ₂ (L ¹)(N ₃) ₄]H ₂ O	Pale brown	70	327 ^a	18.91 (17.89)	31.17 (31.28)	3.19 (3.28)	33.91 (31.92)	Nil	18.47
[Fe ₂ (L ¹)(N ₃) ₄]H ₂ O	Brown	81	206 ^a	18.98 (18.67)	31.36 (32.13)	2.84 (3.03)	33.80 (32.79)	Nil	12.67
[Co ₂ (L ¹)(N ₃) ₄]H ₂ O	Blue	67	329	18.73 (19.51)	31.27 (31.80)	2.85 (3.00)	32.17 (32.45)	Nil	17.13
[Ni ₂ (L ¹)(N ₃) ₄]H ₂ O	Green	71	322 ^a	19.54 (19.44)	30.81 (31.83)	2.95 (3.00)	33.48 (32.48)	Nil	14.78
[Cu ₂ (L ¹)(N ₃) ₄]	Green	75	325 ^a	21.03 (21.34)	32.65 (32.27)	2.56 (2.71)	32.93 (32.56)	Nil	12.11
[Zn ₂ (L ¹)(N ₃) ₄]H ₂ O	Pale Yellow	81	303 ^a	21.17 (21.19)	30.97 (31.14)	2.79 (2.94)	31.29 (31.77)	Nil	18.24
[Cd ₂ (L ¹)(N ₃) ₄]H ₂ O	White	73	319 ^a	30.76 (31.61)	31.68 (32.09)	2.89 (3.03)	32.07 (32.75)	Nil	11.54
L ²	Dark yellow	52	266–268	–	65.23 (65.84)	5.93 (6.14)	8.37 (8.53)	Nil	–
[Cr ₂ (L ²)(N ₃) ₄]Cl ₂ ·H ₂ O	Green	69	267 ^a	14.16 (15.09)	30.94 (31.36)	3.15 (3.22)	27.66 (28.45)	11.42 (10.29)	73.01
[Mn ₂ (L ²)(N ₃) ₄]H ₂ O	Pale yellow	75	244 ^a	17.94 (17.60)	33.67 (34.63)	3.31 (3.55)	32.34 (31.41)	Nil	13.52
[Fe ₂ (L ²)(N ₃) ₄]	Brown	74	233 ^a	17.61 (18.37)	33.57 (33.55)	3.18 (3.31)	32.12 (32.25)	Nil	15.64
[Co ₂ (L ²)(N ₃) ₄]H ₂ O	Blue	83	330 ^a	17.96 (18.64)	33.83 (34.19)	3.24 (3.51)	30.48 (31.01)	Nil	19.82
[Ni ₂ (L ²)(N ₃) ₄]H ₂ O	Green	79	293 ^a	18.92 (18.58)	33.06 (34.22)	3.32 (3.51)	31.95 (31.04)	Nil	13.46
[Cu ₂ (L ²)(N ₃) ₄]H ₂ O	Green	72	229 ^a	20.03 (19.81)	32.43 (33.70)	3.26 (3.46)	31.45 (30.57)	Nil	18.63
[Zn ₂ (L ²)(N ₃) ₄]	White	73	253	21.38 (20.85)	34.15 (34.47)	3.09 (3.21)	31.14 (31.26)	Nil	17.07
[Cd ₂ (L ²)(N ₃) ₄]	White	69	309 ^a	29.96 (31.17)	29.43 (29.97)	2.38 (2.79)	26.94 (27.19)	Nil	17.15

^aDecomposed.**Scheme 1.** General structures of the ligands.

4.2. IR and NMR spectra

The IR spectra of the free ligands show characteristic bands due to the $\nu_{\text{as}}(\text{COO})$, $\nu_{\text{s}}(\text{COO})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ functional groups (see supporting information (SI), Figures SI 5 and SI 6). The peaks around 1632, 1458 and 1614, 1416 cm^{-1} assigned for $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ for L¹ and L², respectively [14]. Bands detected around 1600 and 1570 cm^{-1} are due to the $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$, respectively [15]. The IR spectra of the

complexes exhibited L¹ and L² bands with the appropriate shifts and the M–O and M–N frequencies due to the complex formation (Table 2). Upon complexation, the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ of the carboxylato vibration are shifted and observed to be around 1601–1628 and 1400–1462 for the L¹ and 1593–1620 and 1412–1423 cm^{-1} for the L² complexes, respectively, indicating coordination of the carboxylate group to the metal atoms (see supporting information, Figures SI 7 and SI 8). These



Where M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

Scheme 2. General structure of the proposed polymeric complexes, where M=Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

bands were shifted to lower frequency compared with that in the free ligands, except that for $[Ni_2^{II}(L^2)(N_3)_4]H_2O$ and $[Cu_2^{II}(L^2)(N_3)_4]H_2O$ complexes which shifted to higher frequency. This can be attributed to delocalization of metal electron density (t_{2g}) to the π -system of the ligand [16]. However, shifting to higher frequency may attribute to weak interaction between the carboxylato group and the metal ion. The fashion and the shape of the bands refer to the coordination of the oxygens of carboxylato moieties with the metal atoms [17]. The difference between $\nu_{as}(COO)$ and $\nu_s(COO)$ is characteristic of a bidentate coordination mode [18,19]. The IR

spectra of the complexes exhibited new bands around 2041–2093 and 1318–1369 cm^{-1} which were assigned to the asymmetric $\nu_{as}(N_3)$ and symmetric vibration $\nu_s(N_3)$ of the azido moiety, suggesting the EO bridging mode with metal ion with $N(\mu_{-1,1})$ fashion [20,21]. At lower frequency, the complexes exhibited bands around 498–606 and 406–444 cm^{-1} which were assigned to $\nu(M-O)$ and $\nu(M-N)$, respectively [22].

The 1H and ^{13}C -NMR spectra of the ligands displayed signals corresponding to the various proton and carbon nuclei (see Section 2). The 1H NMR spectra of the ligands show peaks around 2.30, and 4.70 ppm assigned for the ($-CH_2$) groups. Peaks related to the pyridyl groups were detected around 8.0–9.0 ppm (see supporting information, Figures SI 9 and SI 10). ^{13}C -NMR spectra for the ligands show chemical shifts around 30 ppm attributed to the ($-CH_2$) aliphatic carbon, which was observed as expected at a lower chemical shift. Peaks detected around 60 ppm are characteristic of carbon attached to the nitrogen of the pyridyl moiety ($-CH_2-N$). Signal around 175 ppm is assigned to the ($C=O$) of the carboxylato group, and indicates that the two carboxylato moieties are equivalent (see supporting information, Figures SI 11 and SI 12).

The 1H NMR spectrum for $[Cd_2(L^2)(N_3)_4]$ displays peaks at $\delta = 2.15$ and 2.35 ppm, related to the methylene groups for ($C_{3,3}-H$ and $C_{2,2}-H$), respectively (see supporting information, Figure SI 13). The latter signal is shifted to upfield, compared with that in the free ligand, due to the increase in the electron density. This

Table 2. IR frequencies (cm^{-1}) of the compounds.

Compound	$\nu_{as,s}(C=O)$	$\nu(C=N)$	$\nu(C=C)$	$\nu(M-O)$	$\nu(M-N)$	$\Delta(\nu_{as}-\nu_s)$
L^1	1632, 1458	1597	1578	–	–	174
$[Cr_2^{II}(L^1)(N_3)_4]Cl_2H_2O$	1620, 1420	1595	1595	536, 562	424	200
$[Mn_2^{II}(L^1)(N_3)_4]H_2O$	1609, 1418	1572	1543	505, 561	419	191
$[Fe_2^{II}(L^1)(N_3)_4]H_2O$	1617, 1400	1610	1610	536, 63	406	217
$[Co_2^{II}(L^1)(N_3)_4]H_2O$	1607, 1416	1570	1570	546, 565	419	191
$[Ni_2^{II}(L^1)(N_3)_4]H_2O$	1605, 1416	1636	1551	598, 563	432	189
$[Cu_2^{II}(L^1)(N_3)_4]$	1628, 1412	1593	1582	501, 532	440	216
$[Zn_2^{II}(L^1)(N_3)_4]H_2O$	1611, 1416	1533	1533	536, 567	422	195
$[Cd_2^{II}(L^1)(N_3)_4]H_2O$	1601, 1418	1638	1560	500, 565	444	183
L^2	1614, 1416	1603	1568	–	–	198
$[Cr_2^{II}(L^2)(N_3)_4]Cl_2H_2O$	1593, 1412	1628	1582	532, 575	440	181
$[Mn_2^{II}(L^2)(N_3)_4]H_2O$	1610, 1416	1603	1603	565	419	194
$[Fe_2^{II}(L^2)(N_3)_4]$	1595, 1412	1632	1632	498, 562	419	183
$[Co_2^{II}(L^2)(N_3)_4]H_2O$	1607, 1416	1568	1568	507, 564	432	191
$[Ni_2^{II}(L^2)(N_3)_4]H_2O$	1620, 1420	1597	1597	536, 606	424	200
$[Cu_2^{II}(L^2)(N_3)_4]H_2O$	1609, 1418	1634	1535	507, 563	436	191
$[Zn_2^{II}(L^2)(N_3)_4]$	1611, 1416	1638	1564	498, 567	420	195
$[Cd_2^{II}(L^2)(N_3)_4]$	1601, 1416	1633	1566	534, 565	415	185

Table 3. Magnetic moment and UV–VIS spectral data in DMSO solutions.

Compound	μ_{eff} (BM) (per atom)	Band position (λ nm)	Extinction coefficient ϵ_{max} ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	Assignments
[Cr ₂ ^{II} (L ¹)(N ₃) ₄]Cl ₂ · H ₂ O	2.44	263	1785	$\pi \rightarrow \pi^*$
		467	4	$^4\text{A}_{2\text{g}}(\text{F}) \rightarrow ^4\text{T}_{2\text{g}}(\text{F})$ (ν_1)
		756	3	$^4\text{A}_{2\text{g}}(\text{F}) \rightarrow ^4\text{T}_{1\text{g}}(\text{F})$ (ν_2)
[Mn ₂ ^{II} (L ¹)(N ₃) ₄] · H ₂ O	3.03	268	2150	$\pi \rightarrow \pi^*$
		362	21	CT
		643	4	$^6\text{A}_{1\text{g}}(\text{S}) \rightarrow ^4\text{T}_{1\text{g}}(\text{G})$
[Fe ₂ ^{II} (L ¹)(N ₃) ₄] · H ₂ O	0.79	272	2144	L.F
		362	206	CT
		586	21	$\text{T}_{2\text{g}} \rightarrow \text{A}_{1\text{g}}$
[Co ₂ ^{II} (L ¹)(N ₃) ₄] · H ₂ O	1.77	270	2036	L.F
		346	129	CT
		633	61	$^4\text{T}_{1\text{g}}(\text{F}) \rightarrow ^4\text{A}_{2\text{g}}(\text{F})$
[Ni ₂ ^{II} (L ¹)(N ₃) ₄] · H ₂ O	1.55	677	73	$^4\text{T}_{1\text{g}}(\text{F}) \rightarrow ^4\text{A}_{2\text{g}}(\text{F})$
		266	758	L.F
		303	124	C.T
[Cu ₂ ^{II} (L ¹)(N ₃) ₄]	1.08	633	53	$^3\text{T}_{2\text{g}} \rightarrow ^3\text{T}_{1\text{g}}(\text{F})$
		268	350	L.F
		611	50	$^2\text{B}_{1\text{g}} \rightarrow ^2\text{B}_{2\text{g}}$
[Zn ₂ ^{II} (L ¹)(N ₃) ₄] · H ₂ O	Diamagnetic	266	1443	L.F
[Cd ₂ ^{II} (L ¹)(N ₃) ₄] · H ₂ O	Diamagnetic	265	723	L.F
[Cr ₂ ^{II} (L ²)(N ₃) ₄]Cl ₂ · H ₂ O	1.84	287	2062	$\pi \rightarrow \pi^*$
		462	15	$^4\text{A}_{2\text{g}}(\text{F}) \rightarrow ^4\text{T}_{2\text{g}}(\text{F})(\text{V1})$
		670	13	$^4\text{A}_{2\text{g}}(\text{F}) \rightarrow ^4\text{T}_{1\text{g}}(\text{F})(\text{V2})$
[Mn ₂ ^{II} (L ²)(N ₃) ₄] · H ₂ O	2.89	264	1455	L.F
		376	64	C.T
		459	48	$^6\text{A}_{1\text{g}}(\text{F}) \rightarrow ^4\text{T}_{2\text{g}}(\text{G})$
[Fe ₂ ^{II} (L ²)(N ₃) ₄]	1.97	552	13	$^6\text{A}_{1\text{g}}(\text{S}) \rightarrow ^4\text{T}_{1\text{g}}(\text{G})$
		269	970	$\pi \rightarrow \pi^*$
		450	91	$^5\text{A}_{2\text{g}} \rightarrow \text{T}_{2\text{g}}$
[Co ₂ ^{II} (L ²)(N ₃) ₄] · H ₂ O	1.87	675	45	$^5\text{T}_{2\text{g}} \rightarrow ^5\text{E}_{\text{g}}$
		263	663	L.F
		607	50	$^4\text{T}_{1\text{g}}(\text{F}) \rightarrow ^4\text{T}_{1\text{g}}(\text{P})$
[Ni ₂ ^{II} (L ²)(N ₃) ₄] · H ₂ O	1.16	634	57	$^4\text{T}_{1\text{g}}(\text{F}) \rightarrow ^4\text{A}_{2\text{g}}(\text{F})$
		276	1053	$\pi \rightarrow \pi^*$
		662	9	$^3\text{T}_{2\text{g}} \rightarrow ^3\text{T}_{1\text{g}}(\text{F})$
[Cu ₂ ^{II} (L ²)(N ₃) ₄] · H ₂ O	0.89	734	7	$^3\text{B}_{1\text{g}} \rightarrow ^3\text{B}_{2\text{g}}$ and $^3\text{B}_{1\text{g}} \rightarrow ^3\text{A}_{2\text{g}}^{\text{a}}$
		270	2087	L.F
		622	150	$^2\text{B}_{1\text{g}} \rightarrow ^2\text{B}_{2\text{g}}$
[Zn ₂ ^{II} (L ²)(N ₃) ₄]	Diamagnetic	268	1744	$\pi \rightarrow \pi^*$
[Cd ₂ ^{II} (L ²)(N ₃) ₄]	Diamagnetic	269	1172	$\pi \rightarrow \pi^*$

Note: CT, charge transfer.

may be attributed to the fact that, upon complexation, each carboxylato group becomes almost co-planar with the CH₂ group and the pyridinium molecule. The signal at the chemical shift at 4.65–4.68 ppm is assigned to (C_{4,4-}-H). Signals at chemical shifts at 8.72–8.75 and 9.22–9.24 ppm are assigned to (C_{6,6-},8,8--H) and (C_{5,5-},9,9--H), respectively. These signals are shifted to downfield compared with that in the free ligand. This may be due to the co-planar between the pyridinium and the carboxylato anion groups and leads to the increase in the electron density over the pyridinium group. The

¹³C-NMR spectrum for [Cd₂^{II}(L²)(N₃)₄] shows chemical shifts at $\delta = 29.34$ and 33.99 ppm, assigned to (C_{3,3-}) and (C_{2,2-}), respectively (see supporting information, Figure SI 14). The spectrum showed the peak of the (C_{4,4-}) downfield and observed it at 65.52 ppm, compared with that in the free ligand. The chemical shift of the C=O group of the carboxylato moiety appears as expected downfield at $\delta = 178.11$ ppm. This signal is shifted downfield, compared with that in the free ligand at 173.38 ppm, due to the coordination of the carboxylato moiety with Cd(II) ion.

4.3. Mass spectra

The mass spectra of the ligands were also consistent with the proposed structural formulae (see Section 2 and supporting information, Figures SI 15-17). The positive ion ES mass spectra for several complexes were reported. The mass spectrum of $[\text{Co}_2(\text{L}^1)(\text{N}_3)_4] \cdot \text{H}_2\text{O}$ showed several peaks corresponding to successive fragmentations of the molecule (see supporting information, Figure SI 18). The complex showed a peak at m/z 604.86 (7%) (M^+) which represents the molecular ion peak of the complex. Other distinct peaks were observed in the mass spectrum at m/z 444.73 (5%), 418.72 (10%), 352.64 (56%), 336.65 (100%), 284.60 (5%) and 202.56 (3%) assigned to the $(\text{M}-(2\text{N}_2 + 2\text{CO} + \text{CH}_4 + \text{N}_2\text{H}_4))^+$, $(\text{M} - (2\text{N}_2 + 2\text{CO} + \text{CH}_4 + \text{N}_2\text{H}_4 + \text{CN}))^+$, $(\text{M}-(2\text{N}_2 + 2\text{CO} + \text{CH}_4 + \text{N}_2\text{H}_4 + 2\text{CN} + \text{C}_3\text{H}_4))^+$ and $(\text{M}-(2\text{N}_2 + 2\text{CO} + \text{CH}_4 + \text{N}_2\text{H}_4 + 2\text{CN} + \text{C}_3\text{H}_4\text{O}))^+$, $(\text{M}-(2\text{N}_2 + 2\text{CO} + \text{CH}_4 + \text{N}_2\text{H}_4 + 2\text{CN} + \text{C}_3\text{H}_4\text{O} + \text{C}_2\text{H}_2 + \text{CN}))^+$, and $(\text{M}-(2\text{N}_2 + 2\text{CO} + \text{CH}_4 + \text{N}_2\text{H}_4 + 2\text{CN} + \text{C}_3\text{H}_4\text{O} + \text{C}_2\text{H}_2 + \text{CN} + \text{N}_4 + \text{CN}))^+$ fragments, respectively. The spectrum of $[\text{Zn}_2(\text{L}^1)(\text{N}_3)_4] \cdot \text{H}_2\text{O}$, displayed a peak at $m/z = 617.53$ (M^+) (7%) which represents the molecular ion peak of the complex. Other distinct peaks were observed in the mass spectrum at m/z 545.42 (3%), 405.00 (6%), 332.98 (8%), 229.09 (24%), 188.18 (47%) and 157.18 (100%) related to the $(\text{M}-(\text{N}_2 + \text{N}_2\text{O}))^+$, $(\text{M}-(3\text{N}_2 + \text{CO} + \text{CH}_2\text{CH}_2))^+$, $(\text{M}-(\text{CH}_2\text{CH}_2 + \text{CO}_2))^+$ and $(\text{M}-(2\text{CN} + 2\text{CH}_9\text{CH}))^+$, $(\text{M}-(2\text{CN} + 2\text{CH}_9\text{CH} + \text{C}_3\text{H}_5))^+$, and $(\text{M}-(2\text{CN} + 2\text{CH}_9\text{CH} + \text{C}_3\text{H}_5 + \text{N}-\text{OH}))^+$ fragments, respectively. These results are similar to those of analogous complexes that were reported earlier by others [23]. The mass spectrum of $[\text{Mn}_2(\text{L}^2)(\text{N}_3)_4] \cdot \text{H}_2\text{O}$ (see supporting information, Figure SI 19) shows the following ion peaks at $m/z = 624.23$ (M^+) (4%), 594.23 (7%), 532.20 (13%), 515.17 (3%), 445.12 (28%), 371.09 (40%), 302.02 (100%) and 198.92 (16%) assigned to $[\text{M}-(\text{NO})]$, $[\text{M}-(2\text{NO} + \text{N}_2\text{H}_4)]$, $[\text{M}-(2\text{NO} + \text{N}_2\text{H}_4 + \text{NH}_3)]$, $[\text{M}-(2\text{NO} + \text{N}_2\text{H}_4 + \text{NH}_3 + \text{CH}_2\text{N}_4)]$, $[\text{M}-(2\text{NO} + \text{N}_2\text{H}_4 + \text{NH}_3 + \text{CH}_2\text{N}_4 + \text{N}_2\text{H}_2 + \text{CO}_2)]$, $[\text{M}-(2\text{NO} + \text{N}_2\text{H}_4 + \text{NH}_3 + \text{CH}_2\text{N}_4 + \text{N}_2\text{H}_2 + \text{CO}_2 + \text{CO} + \text{C}_3\text{H}_5)]$ and $[\text{M} - (2\text{NO} + \text{N}_2\text{H}_4 + \text{NH}_3 + \text{CH}_2\text{N}_4 + \text{N}_2\text{H}_2 + \text{CO}_2 + \text{CO} + \text{C}_3\text{H}_5 + \text{C}_6\text{H}_6\text{CN})]$, respectively.

4.4. Electronic spectra, magnetic moments and conductivity measurements

The UV-VIS spectra of L^1 and L^2 exhibit an intense absorption peak at 279 and 267 nm, respectively, assigned to overlap of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The electronic spectra of the complexes of L^1 exhibited various extents of hypsochromic shift of the bands related

to the intra-ligand ($\pi \rightarrow \pi^*$) transition in the Cr(III) and Mn(II), and ligand field in other complexes (Table 3). Bands related to the (CT) transition were observed in the spectra of the complexes (Table 3). The electronic spectrum of the Cr(III) complex displayed two additional bands, which could be attributed to the spin allowed d-d transitions $^4\text{A}_2\text{g}^{(\text{F})} \rightarrow ^4\text{T}_2\text{g}^{(\text{F})}$ (ν_1), $^4\text{A}_2\text{g}^{(\text{F})} \rightarrow ^4\text{T}_1\text{g}^{(\text{F})}$ (ν_2) [24,25]. The band $^4\text{A}_2\text{g}^{(\text{F})} \rightarrow ^4\text{T}_1\text{g}^{(\text{P})}$ (ν_3), transition may be at higher frequency and hidden by the (CT) or ligand band. These data together with the magnetic moment indicate an octahedral geometry around the Cr(III) atom [26]. The Mn(II) complex showed the $\pi \rightarrow \pi^*$ (CT) transitions and an additional peak at 643 nm assigned to the d-d transition in a distorted octahedral geometry [24-26]. The observed magnetic moment of this complex is typical for a high-spin octahedral structure of polymeric Mn(II) complex. The electronic spectra of the Fe(II) and Co(II) complexes are consistent with the octahedral assignment [24,27]. The magnetic moment of these complexes is typical for a high-spin octahedral structure. The Ni(II) complex is paramagnetic suggesting a distorted octahedral geometry [27]. The electronic spectrum of this complex, as well as the other analytical data, was consistent with this assignment. The spectrum of the Cu(II) complex in DMSO exhibited one low-intensity band which is characteristic of distorted octahedral Cu(II) complexes. The magnetic moment value of the green Cu(II) complex, as well as the other analytical data, is in agreement with a distorted octahedral structure [28-30]. The spectra of the Zn(II) and Cd(II) complexes exhibited bands assigned to the ligand field [24]. These complexes are diamagnetic as expected for the d^{10} system. The electronic spectra of the complexes of L^2 exhibited bands were related to the intra-ligand ($\pi \rightarrow \pi^*$) and the (CT) transitions (Table 3). The spectra of the Cr(III) and Mn(II) complexes of L^2 showed similar behavior to those of L^1 suggesting octahedral geometries for the complexes. The magnetic moment values were consistent with the octahedral structures. The spectra of Zn(II) and Cd(II) complexes of L^2 showed similar behavior to those of L^1 suggesting octahedral geometries [24]. The molar conductivities indicate that the Cr(III) complex is a 1:2 electrolyte, while the other complexes are non-electrolyte (Table 1) [31,32].

The magnetic moment values for the complexes at RT are lower than the predicted values. This may arise from metal-metal interactions or extensive electron delocalization, which may be related to the formation of polymeric structures [27].

5. Conclusion

In this paper, we have investigated the synthesis and coordination chemistry of some polymeric complexes obtained

from the reaction of the dicarboxylato ligands L¹ and L² and azido moiety with some metal ions. The mode of bonding and overall structure of the complexes were determined through physico-chemical and spectroscopic methods. These studies revealed the formation of polymeric complexes bearing mixed bridges of carboxylato and azido moieties. In these complexes, the geometries about metal centers are a distorted octahedral.

Supplemental data

Supplemental data for this article can be accessed [doi:10.1080/2164232X.2014.883290](https://doi.org/10.1080/2164232X.2014.883290)

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