Manganese (II) complexes containing carbacylamidophosphate ligands: Synthesis, molecular structures and computational investigation

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Manganese (II) complexes containing carbacylamidophosphate ligands: Synthesis, molecular structures and computational investigation

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ABSTRACT

Two carbacylamidophosphates ligands, 4-NC5H4C(O)NHP(O)R2, [where R = cyclopentylamine (L1) and tert-butylamine (L2)] were used to synthesize their Mn(II) complexes, C1 and C2. The crystal structures of the C1 and C2 complexes were determined by single crystal X-ray diffraction techniques. X-ray crystallography analysis revealed that C1 and C2 are crystallized in the monoclinic C2/c and P21/n space groups, respectively. The results indicated that these similar ligands have different coordination patterns. Ligand L1 acts as a bidentate bridging ligand via the oxygen atom of the phosphoryl group and the nitrogen atom of the pyridine cycle. Quantum chemical studies were also performed to interpret two different coordination behavior of the ligands, using B3LYP/def2-TZVP level of theory.

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1. Introduction

The synthesis and characterization of coordination polymers are of interest to scientists due to their intriguing structures and useful application potential [1]. Coordination polymers are metal-ligand compounds that extend “infinitely” into one, two, or three dimensions (1D, 2D, or 3D, respectively) via a bridging organic ligand. Carbacylamidophosphates with a pyridine ring in their skeleton are valuable groups of these types of ligands [2–5].

Carbacylamidophosphates (the compounds with a peptide-like group, C(O)NHP(O)) have extensive applications such as anticancer treatments [6,7], produgs [8,9], urea inhibitors [10] and coordination molecules [11,12]. The coordination patterns of carbacylamidophosphate ligands depend on the position of the C=O and P=O groups. The neutral form of these ligands (with the anti-position of mentioned groups) usually coordinates via the oxygen atom of the phosphor group [2]. Whereas, the anionic form is obtained by losing the amicid hydrogen, makes the chelate complex through the oxygen atoms of phosphor and carbonyl groups in syn conformation [13–16]. However, few chelate complexes have been reported in the neutral form of the ligand up to now as bidentate [17,18] and bridged bidentate ligands [19]. Also there are limited structures with a gauche orientation of C=O versus P=O [20]. Although various phosphoramidate complexes with transition metals have been structurally investigated, limited complexes of carbacylamidophosphate including isonicotinamide have been reported [2–5], and the different coordination pattern of these complexes by changing the type of metal and ligand is not well known yet. In this work, two carbacylamidophosphate ligands including isonicotinamide with 4-NC5H4C(O)NHP(O)R2 formula, in which R = NH(CH3)2 (L1), and R = NHC(CH3)2 (L2) [21] were used to synthesize Mn(II) complexes with general formula, MnC3L2, where L = L1 (in C1); L = L2 (in C2). The crystal structure of C1 and C2 complexes were determined by X-ray crystallography. To survey the reasons of observed coordination behaviors of L1 and L2, structural and electronic parameters of free ligands were firstly studied by structural parameters, MESP and NBO analyses. Secondly, the character of metal-ligand interaction was explored by AIM analysis.

2. Results and discussion

2.1. NMR and IR study

Synthesis of ligands L1 and L2 were performed according to the
literature [21], C1 and C2 complexes were obtained from the reaction of L1 and L2 with MnCl2 (Scheme 1).

The selected spectroscopic data of the synthesized compounds are given in Table 1. IR and NMR spectra of the ligands and complexes are demonstrated in Figs. S1–S12. The downfield chemical shift (δ) of 31P in L1 (6.40 ppm) in comparison with L2 (2.18 ppm) reveals the more electron donating property of cyclopentylamine. Because of the low solubility of C1 and C2 in common NMR solvents such as CDCl3, CD3OD, (CD3)2CO, (CD3)2SO, the peak of phosphorous and carbon atoms have not been observed. Owing to the paramagnetic properties of the manganese ion, 1H NMR spectra of C1 and C2 complexes are broadened and no splitting has been specified.

In IR spectra, the phosphoryl group of compounds L2 and C2 are shown as a doublet band. This doublet structure is seen for 31P in some phosphoryl compounds, which may be due to the molecular association, conformation in homogeneity, overlap from other bands, Fermi resonance and Davydov splitting in crystals [22]. As seen in Table 1, these frequencies of L2 and C2 are close to each other while the IR spectra of C1 reveals a large decreasing for Cu(P=O) compared with the data for the free ligand, L1. This observation gave us an idea about the coordination of L1 from the P=O site. On the other hand, the IR spectra of C1 and C2 show an increasing for the main vibrational frequencies of the pyridine ring (the ring stretching and planar ring deformation) [23,24] in comparison to their related ligands (from 1599, 507 cm−1 in L1 to 1613, 523 cm−1 in C1 and 1601, 543 cm−1 in L2 to 1613, 553 cm−1 in C2, respectively). As shown in Table 1, this increasing of mentioned frequencies is observed in complexes which coordination of ligand occurs from the N of pyridine ring [2,22]. Thus, we can predicate that L1 coordinates via Npyridine and P=O sites, whilst L2 acts as a monodentate ligand through the nitrogen of pyridine ring. These predictions are confirmed by the X-ray crystallographic structures of C1 and C2 in the following sections.

2.2. Electronic spectra study

A comparison of the electronic spectra of C1, C2, and their related ligands, L1 and L2 showed that λmax of the ligands (213.5 and 202.0 nm) is shifted to a longer wavelength (221.0 and 232.8 nm) after complexation (Table 1). These results are in good agreement with the reported data for the similar complexes assigned to π → π* intra-ligand transition [2].

2.3. X-ray crystallography investigation

A single crystal of C1 was obtained from ethanol/acetonitrile mixture and that of C2 from ethanol after slow evaporation at room temperature. The crystal data and the details of the X-ray analysis are given in Table 2, selected bond lengths and angles in Table 3, and hydrogen bonding data in Table 4. Molecular structures of these compounds are shown in Fig. 1.

C1 and C2 crystallize in the monoclinic system with C2/c and P21/n space groups, respectively. The crystal structures of these complexes exhibited different coordination patterns (Fig. 1).

The carbacylamidophosphate, L1, acts as a bidentate bridging ligand via the oxygen atom of the phosphoryl group and the nitrogen atom of the pyridine between two Mn atoms in C1. This leads to a two-dimensional polymer framework which is parallel to ab plane (Fig. 2). Each Mn atom can be considered as a four-connected node, topologically. The joining of Mn atoms (nodes) by the L1 linkers forms a two-dimensional sheet structure with a sql/Shubnikov tetragonal plane net (Fig. 2 (a) and (b)). Adjacent 2D layers are further interconnected by inter-layer contacts. As it can be seen
The coordination of ligand to Mn causes an increase in the bond length from 2.3174 Å that is about 0.02 Å shorter than its analogous complex (2.3384 Å), while the Mn–C bond length in C1, 2.5114 Å, is longer than the similar bond in C2, 2.4971 Å. A comparison between the crystal structures of C2 and L2 [21] shows that the coordination of ligand to Mn causes an increase in P–Namide, pyridine–C, and C=O bond lengths (about 0.023 Å, 0.018 Å and 0.011 Å, respectively) and a negligible decrease in P–Namide and P=O bond lengths (about 0.008 Å and 0.006 Å, respectively).

Crystal structures of C1 and C2 complexes illustrate that the P=O and C=O groups have an anti-configuration. The bond angles around the phosphorus atom (102.92–115.86° in C1 and 104.18–115.44° in C2) demonstrate a nearly tetrahedral configuration for this atom. The P–Namide bond lengths (1.6983 Å and 1.7173 Å in C1 and 1.6225 Å and 1.623 Å in C2) are longer than the P–Namide ones (about 1.6225 Å and 1.623 Å in C1 and C2, respectively), while C–Namide bond lengths (1.351 Å in C1 and 1.341 Å in C2) are shorter than C–Namide (1.475 Å and 1.493 Å in C1 and C2, respectively). The reason for these observations is related to the electrostatic interaction between the lone pair of Namide and antibonding π orbital of carbonyl, which causes a partial double bond in C–Namide [25, 26]. All of the mentioned P–N bonds are shorter than reported P–N single bond (1.777 Å) [27] that is probably owing to the electrostatic effects (polar bonds) which overlap with P–N σ-bond [28]. The bond angles around the nitrogen atoms (P–N–H, P–N–C, and C–N–H) indicate that the environment of this atoms are nearly planar (sums of the mentioned angles are 354°–360°).
Table 3
Selected bond lengths (Å) and bond angles (°) for the structures of C₁ and C₂.

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<tr>
<th>Bond length (Å)</th>
<th>C₁</th>
<th>C₂</th>
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<tr>
<td>Mn₁–O₁ (1)</td>
<td>2.1304 (11)</td>
<td>2.1988 (18)</td>
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<td>Mn₁–N₁ (4)</td>
<td>2.3174 (13)</td>
<td>2.3384 (18)</td>
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<tr>
<td>Mn₁–Cl₁ (1)</td>
<td>2.5114 (4)</td>
<td>2.4971 (5)</td>
</tr>
<tr>
<td>Mn₂–Oₒ (1)</td>
<td>1.6194 (16)</td>
<td>1.622 (2)</td>
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<tr>
<td>Mn₂–N₄ (4)</td>
<td>1.6300 (17)</td>
<td>1.624 (2)</td>
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<tr>
<td>Mn₂–Cl₃ (1)</td>
<td>1.7014 (16)</td>
<td>1.7173 (19)</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Bond angles (°)</th>
<th>C₁</th>
<th>C₂</th>
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<tr>
<td>O₁#1–Mn₁–O₁#2</td>
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<td>Cl₁–Mn₁–Cl₁#3</td>
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<tr>
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<td>115.86 (10)</td>
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<tr>
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<td>102.43 (8)</td>
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<tr>
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<td>105.36 (8)</td>
<td>105.86 (10)</td>
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<tr>
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<td>115.45 (10)</td>
<td>109.26 (10)</td>
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<td>O₂–P₂–N₁ (4)</td>
<td>111.53 (8)</td>
<td>109.23 (10)</td>
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<tr>
<td>O₂–P₂–N₁ (3)</td>
<td>115.45 (10)</td>
<td>109.23 (10)</td>
</tr>
</tbody>
</table>

C₁ has a hydrogen bonding N (2)–H (2) … O (2) between the amine hydrogen and carbonyl oxygen atom as well as two hydrogen bonding interactions, N (1)–H (1) … Cl (1) and N (3)–H (3) … Cl (1). The P=O–H–N hydrogen bond is not observed in this compound because of replacing the mentioned hydrogen bond with P=O … M covalent bond. The strength of a hydrogen bond increases as the H–Cl and N–Cl distances decrease and the bond angle <(NCl) approaches linearity [180°] [Table 4]. A three-dimensional polymeric cluster is produced by four intermolecular hydrogen bonds N (2):H (1 N) … O (2), O (3):H (30) … O (1), N (3):H (3 N) … Cl (1) and N (4):H (4 N) … Cl (1) in complex C₂.

2.4. Theoretical studies

Ligands studied here have the general formula C₆H₅C(O)NHP(O)(R₂) (Scheme 1), in which R=cyclopentyl (in L₁) and tert-butylamine (in L₂). In the complexation procedure of mentioned ligands with Mn(II) metal ion, two different structures were seen [Fig. 1]. In the case of L₁, both pyridinic-nitrogen and the oxygen of phosphoryl group simultaneously coordinated to two different metal ions, which led to a polymeric complex; but in L₂, the donor atom, which coordinated to Mn(II) is just the pyridinic-nitrogen, that led to a single crystal (Scheme 2).

The steric environment of the phosphoryl group in these two ligands is an important issue. Taking into account the different steric volumes of cyclopentyl and tert-butyl groups may lead to this conclusion that the greater steric hindrance of tert-butylamine rather than cyclopentylamine is the only reason of different observed coordination behaviors in L₁ and L₂. The optimized space-filling structure of these ligands illustrates the different steric hindrance of substituted groups in L₂ than L₁ (Fig. 3).

The relatively more steric hindrance of tert-butylamine in L₂ than cyclopentylamine in L₁ is observable in Fig. 3, but it doesn’t seem to be the only significant reason for the different coordination behavior of these ligands. In addition to the steric effects and to rationalize the influence of these different substituted R–groups on the coordination behavior of L₁ and L₂, and furthermore the nature of metal-ligand interaction, some computational efforts were done. First of all, we surveyed the structural and electronic parameters of free ligands to scrutinize their differences, which led to different coordination behaviors.

2.4.1. Structural parameters

P=O and N = C (pyridinic-nitrogen) calculated bond lengths in
Fig. 1. The ORTEP diagram of C1 and C2. Ellipsoids are drawn at the 50% probability level. Symmetry codes: i: 1/2 + x, 1/2 - y, z; ii: -x, y, 1/2 - z; iii: 1/2 - x, 1/2 + y, 1/2 - z; iv: -1/2 + x, 1/2 + y, z; v: -1/2 + x, -1/2 + y, z; vi: 1-x, 1-y, 2-z.

Fig. 2. (a) 2D layer structure of compound C1 (parallel to ab plane); (b) Topology view of the 2D layers in C1, L1 linkers are shown in orange color.
optimized free ligands are presented in Fig. 4 (Cartesian atomic coordinates of \( L_1, L_2, C_1 \) and \( C_2 \) are given in supplementary data, Table S15). In these structures, \( N - C \) bond lengths are the same (1.331 and 1.334 Å), but \( P - O \) bond length in \( L_1 \) is 1.483 Å in comparison with the shorter value in \( L_2 \), 1.474 Å.

2.4.2. Molecular electrostatic potential (MESP) profiles

The electrostatic potential is widely used to analyze the molecular stability and reactivity as well as to identify the reactive sites of the molecule in electrophilic/nucleophilic reactions and hydrogen bonding interactions. Considering the overall molecular charge distribution, every area of the surface is illustrated by different colors. In the MESP maps of this study, the interpolated red map is a representation of electronegative potential and the electropositive potential of strongest repulsion is coded with blue color. The green exhibits the potential halfway between these two extremes. The plots of molecular electrostatic potential (MESP) for synthesized ligands are shown in Fig. 5.

MESP plotted onto constant electron density surface reveals that the most electronegative potential region in both ligands is over the oxygen atom of the phosphoryl group (red color) and the pyridinic-nitrogen atom (orange color). The appearance of the localized negative potential region situated at the nitrogen atom of pyridine ring is consistent with the crystallographic results, which recognized this region as a coordinating part to the Mn\(^{2+}\) cation. In the case of phosphoryl group’s oxygen atom, both ligands can play a role as a donor atom to metal cation according to MESP plot, though this just occurred in \( L_1 \). To interpret this subject, the electronic properties of the P–O bond in both ligands will be scrutinized in the following sections.

2.4.3. NBO analysis

NBO analysis was done on pyridinic-nitrogen and also phosphorus-oxygen interactions to survey the character of

![Scheme 2. Different donor atoms in \( L_1 \) and \( L_2 \).](image)

![Fig. 3. The optimized space-filling structure of studied ligands at B3LYP/def2-TZVP level.](image)

![Fig. 4. Optimized structures of studied ligands at B3LYP/def2-TZVP level of theory.](image)
mentioned bonds, which is an important factor in coordination behavior of these ligands to a metal cation.

2.4.3.1 Bond hybridization. The hybridization of P, O and N in related P=B=O and N = C bonds are illustrated in Table 5. The oxygen atom in P=B=O bond has more p character in L1 (sp 1.59) than L2 (sp 1.67). Furthermore, the hybridization of oxygen lone pair, LP (1), in L1 (sp 0.85) considerably has larger p character than that in L2 (sp 0.56). The p character of the nitrogen atom and its lone pair in both ligands are the same. As can be seen, P=B=O bonds are just composed of sigma (σ) interaction, but this interaction is weaker in L1. Oxygen lone pairs are also freer in L1, which makes it a better donor atom in the coordination process.

2.4.3.2 Wiberg bond index (WBI). Another factor in probing the bond strength is the Wiberg bond index. Wiberg was originally defined for closed-shell and semi-empirical wave functions. For typical chemical bonds, its value is usually very close to formal bond order [29]. Wiberg bond indices of P=B=O and N = C bonds are given in Table 5. WBI values of N = C bonds are equal in both ligands, which demonstrate the bond character is between singlet and doublet (WBI = 1.435). WBI value of P=B=O bond in L2 is more than that of L1 (1.287 and 1.241, respectively) that attests the stronger P=B=O bond in L2 than in L1. This may interpret the better coordination ability of the phosphoryl group’s oxygen in L1.

2.4.3.3 Perturbation theory energy analysis. The other factor which can interpret the strength of the bond is charge transfer. This segment summarizes the second-order perturbative estimates of donor-acceptor (bond-antibond) interactions. This analysis is executed by examining all possible interactions between filled (donor) Lewis-type NBOs and empty (acceptor) non-Lewis NBOs, and estimating their energetic importance by 2nd-order perturbation theory.

As discussed before, investigations on the P=B=O bond lengths, bond hybridizations and bond orders demonstrated greater bond strength in L2. To authenticate mentioned results, the interactions between different atoms’ lone pairs with P=B=O antibonds (σP=B=O* ) are presented in detail in Table 6. These data rationalize the numerical values of the charge transfer from the donor orbitals of nitrogen atoms to BCPS. These data present to σP=B=O* display a considerable discrepancy between L1 and L2 (13.79 and 10.40 kcal mol⁻¹, respectively). Greater values of σP=B=O* to P=B=O antibonding orbital in L1 attenuate the bond, while smaller values in L2 reinforce the bond. Overall, the P=B=O bonds in studied ligands which are involved bonds in complexation with metal cations can be affected by vicinal groups. This investigation illustrates that the cyclopentylamine groups make the P=B=O bond weaker. Thus the oxygen atom would perform a better interaction with metal cation by its lone pairs.

2.4.4 AIM analysis. The AIM analysis is an efficient tool to determine the presence of bond critical points (BCPs). The most often used criteria for the existence of covalent or ionic bonding interactions are the electron density ρ(r) and the Laplacian of the electron density ρ²(r) at the BCPs. The Laplacian of charge density at the BCP (Δ²ρ(BCP)) is the sum of the curvatures in the electron density along any orthogonal coordinate axes at the BCP. The sign of Δ²ρ(BCP) indicates that whether the charge density is locally depleted (Δ²ρ(BCP) < 0) or locally concentrated (Δ²ρ(BCP) > 0). The negative curvatures for λ1 and λ2 at the BCP demonstrates that the electronic charge is locally concentrated within the region inter atoms, which leads to the formation of covalent or polarized bonds and being characterized by large ρ(BCP) values, Δ²ρ(BCP) < 0, and | λ₁/λ₃ | > 1. On the other

<table>
<thead>
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<th>Ligands</th>
<th>Hybridization</th>
<th>O in P=B=O</th>
<th>LP of O</th>
<th>N in N = C</th>
<th>LP of N</th>
<th>WBI P=B=O</th>
<th>WBI N = C</th>
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</thead>
<tbody>
<tr>
<td>L1</td>
<td>sp 1.59</td>
<td>LP (1) sp 0.80</td>
<td>BD (1) sp 1.79</td>
<td>LP (1) sp 2.50</td>
<td>1.241</td>
<td>1.435</td>
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</tr>
<tr>
<td>L2</td>
<td>sp 1.67</td>
<td>LP (1) sp 0.56</td>
<td>BD (1) sp 1.79</td>
<td>LP (1) sp 2.50</td>
<td>1.287</td>
<td>1.435</td>
<td></td>
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</tbody>
</table>

Fig. 5. Molecular electrostatic potential (MESP) maps of L1 and L2.
the positive curvature for $\lambda_3$ at the BCP shows that the electronic density is locally concentrated in each of the atomic basins. In this case, the interaction leads to the formation of highly ionic bonds, hydrogen bonds (HBs) and van der Waals interactions. It is characterized by relatively low $\rho$(BCP) values, $\nabla^2\rho_{\text{BCP}} > \text{Gand } |\lambda_3/|\lambda_3| < 1$. Another calculated value by AIM is ellipticity ($\epsilon$) which is a standard scale for the $\pi$ bond character. The ellipticity at the BCP can be interpreted as a measure of the anisotropy of the electron density. Calculated small values demonstrate minor changes of $\lambda_3$ at the BCP of $N$-bonds and also decrease of $\lambda_3$ considerably when $P$-bonds are coordinated to the metal cation. The analysis was used to determine the presence of bond critical points (BCPs) of the $P=O$ bond in $L_1$ and $L_2$, and also $P=O$, $O$-Mn$^{2+}$ and $N$-$\cdot$Mn$^{2+}$ bonds in related complexes, $C_1$ and $C_2$ (Table 7). This comparison not only forms a dependable vision about the changes of $P=O$ bond character before and after the complexation but also define the nature of $O$-$\cdot$Mn$^{2+}$ and $N$-$\cdot$Mn$^{2+}$ bonds in synthesized complexes.

Calculated AIM charge densities ($\rho$), [$\lambda_3/|\lambda_3|$ and Laplacian ($\nabla^2\rho$) at the $P=O$ BCP and also at the BCP of $O$-$\cdot$Mn$^{2+}$ and $N$-$\cdot$Mn$^{2+}$ interactions are given in Table 7. Minor values of $\rho$ and $|\lambda_3/|\lambda_3|$ at $P=O$ BCP in free ligands ($L_1$ and $L_2$) as well as large positive values of $\nabla^2\rho$, shows weaker covalent character of this bond in the studied ligands. As can be seen, AIM values corroborate that the lower covalent behavior of $P=O$ bond in $L_1$ than $L_2$ makes the phosphoryl oxygen more accessible to coordinate to the metal ion in $L_1$. The charge density at the $P=O$ BCP considerably decreases when $L_1$ is coordinated to the metal cation. The $\rho$ value at the $P=O$ BCP in $L_1$ is 0.207 au but decreases to 0.180 au in $C_1$ complex, $|\lambda_3/|\lambda_3|$ and Laplacian ($\nabla^2\rho$) in accordance with the $\rho$ value confirm that the electrostatic nature of the $P=O$ bond weakens after the complexation. Analysis of the obtained bond critical points for $O$-$\cdot$Mn$^{2+}$ and $N$-$\cdot$Mn$^{2+}$ interactions, suggests a closed-shell and electrostatic character for these interactions. Very small values of $\rho$, $\nabla^2\rho > 0$ and $|\lambda_3/|\lambda_3| \ll 1$ at the BCP of $N$-$\cdot$Mn$^{2+}$ confirm the presence of electrostatic interactions in both complexes.

3. Experimental

3.1. Materials and methods

All reagents and solvents for synthesis were purchased from Merck and used without any further purification.

3.1.1. Spectroscopic measurements

$^1$H, $^13$C and $^{31}$PMNR spectra were recorded on a FT-NMR, Bruker Avance DRS 500 spectrometer. $^1$H and $^13$C chemical shifts were determined relative to TMS, and $^{31}$P chemical shifts were measured relative to 85% H$_3$PO$_4$ where TMS and H$_3$PO$_4$ were acted as external standards. Infrared (IR and FTIR) spectra were recorded on a Shimadzu model IR-60 and FTIR (Thermo Nicolet) Nexus 870 spectrometers. Electronic spectra were recorded on UV-2100 Shimadzu.

3.1.2. X-ray measurements

X-ray data of compound $C_1$ and $C_2$ was collected on a Bruker APEX-II CCD [30] area detector with graphite monochromator Mo Kα radiation ($\lambda = 0.71073$ A). The structures were refined with SHELXTL v. 5.10 [31] by full-matrix least-squares on F2. The hydrogen atoms of NH groups were found in the difference Fourier synthesis and normalized at standard X-ray value 0.90/A.

3.2. Synthesis

3.2.1. Syntheses of ligands

The ligands $L_1$ and $L_2$ were prepared according to the procedure described previously [21].

3.2.2. Synthesis of metal complexes

3.2.2.1. Bis[N-isonicotinyl-n$^0$-bis(cyclopentyl) phosphoric triamide] manganese(II) dichloride ($C_1$). A solution of N-isonicotinyl-N$^0$-N$^0$-bis(cyclopentyl) phosphoric triamide, $L_b$ (0.5 mmol, 0.168 g) was added to a solution of anhydrous manganese chloride (0.25 mmol, 0.031 g) in hot ethanol (20 mL) and stirred at room temperature. After 4 h, 10 mL of acetonitrile was added to the reaction vessel and single crystal of $C_1$ was obtained by slow cooling.

Table 6

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Donor</th>
<th>Acceptor</th>
<th>$\varepsilon^{(2)*}$</th>
<th>$\chi^{(2)}$</th>
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<td>$L_1$</td>
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<td>BD$^*$ (1) P 1$-O$ 2</td>
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<td>13.79</td>
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<td>12.42</td>
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* The values are reported in kcalmol$^{-1}$.

Table 7

Calculated main BCP parameters of $L_1$, $L_2$ and related complexes ($C_1$ and $C_2$) at B3LYP/def2-TZVP level of theory.

| Structure | $\rho$ (in au) | $\nabla^2\rho$ (in au) | $|\lambda_3/|\lambda_3|$ | $\varepsilon$ |
|-----------|---------------|----------------------|------------------|-------------|
| P=$O$     | 0.207         | 1.624                | 0.142            | 0.013       |
| O$\cdot$Mn$^{2+}$ | 0.256         | 1.509                | 0.181            | 0.022       |
| N$\cdot$Mn$^{2+}$ | 0.180, 0.107  | 1.748, 0.908         | 0.172, 0.133     | 0.151       |
| $L_1$     | 0.222         | 0.085                | 0.405            | 0.197       |
| $C_1$     | 0.222         | 0.085                | 0.405            | 0.197       |
| $C_2$     | 0.222         | 0.085                | 0.405            | 0.197       |
evaporation of the solvents at room temperature.

Yield: 90%. Pale pink powder. M. wt.: 798.58; Anal. Calc. for C22H32Cl2MnN8O6P2: C, 45.61; H, 7.42; N, 13.30%. Found: C, 45.81; H, 7.68; N, 13.52%. 1H NMR (500.13 MHz, DMSO-d6): δ = 0.94–1.10 (m, 9H), 4.27–4.56 (b, 1H), 7.81–8.61 (b, 2H). IR (KBr), υ (cm⁻¹): 3397(m), 3151(m), 3097(m), 3045(m), 2965(s), 2929(s), 2873(m), 1670(s), 1654 (s, C=O), 1613(m), 1559(m), 1507(s), 1457(s), 1419(s), 1389(s), 1366(s), 1291(s), 1227(s), 1199 (s, P=O), 1120 (w), 1067(m), 1045(s), 1025(s), 1013(s), 926(w), 891(m), 864(m), 848(m), 818(m), 808(m), 764(m), 707(m), 683(w), 647(m), 523(s), 493(m), 475(m); λmax = 221 nm.

5. Conclusion

Two complexes have been prepared with the carbacylamido-phosphate ligand including isonicotinamidine. This type of ligands has three active sites for coordination with metal (C=O, P=O, and N of pyridine). Therefore, the compound can act as a mono-, bidentate, or bridging ligand. The X-ray crystallographic structure of C1 has shown that L4 acts as a bridging ligand via N of the pyridine ring and oxygen of the P=O group. This complex is a three-dimensional coordination polymer that crystallized in the monoclinic C2/c space group. The Mn(II) ion is six-coordinated center with the first coordination sphere made up of two cis chlorine atoms, and four L4 ligands that two of them are trans phosphoroyl oxygen atoms and others are cis nitrogen of pyridine rings. The second complex, C2, crystallized in the monoclinic P21/n space group. The first coordination sphere of C2 has been made up of two ethanol groups, two chlorine atoms and two phosphoramidates, L2 that are coordinated to the metal through the pyridine ring nitrogen. The greater steric hindrance of L2 than L4 makes the earlier one a monodentate and the later one a bidentate ligand. Different coordination behaviors of L4 and L2 in the complexation procedure have also surveyed computationally by the NBO and AIM analyses. The calculated results unanimously have attested the better coordination ability of the phosphoroyl group’s oxygen in L4 in comparison with L2, which could successfully interpret different coordination behavior of these two ligands.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2018.12.062.

References


