

Dinuclear Molybdenum Tetracarbonyl Complexes of Tetradentate Nitrogen Ligands and Intermolecular Hydrogen Bonding in the Crystal Structure of N,N'-bis-[1-(pyridin-2-yl)ethylidene]-ethane-1,2-diamine

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Multidentate N-ligands (Schiff bases) were prepared by the condensation of

2-acetylpyridine or 2-benzoylpyridine, and 1,2-diaminoethane or 1,6-diaminohexane (2:1 ratio) in ethanol. These ligands were reacted with Mo(CO)₆ to obtain dinuclear metal tetracarbonyl compounds. Both terminal amine groups were seen to form imines from the reaction of mono-ketones with diamines in 2:1 or 1:1 ratios. The structures of these ligands and metal complexes were characterized by elemental analysis, and FT-IR, ¹H-NMR, ¹³C-NMR, and LC-MS spectral techniques. N,N'-bis[1-(pyridin-2-yl)ethylidene]ethane-1,2-diamine, which was obtained by the reaction of 2-acetylpyridine and 1,2-diaminoethane, was also characterized by single crystal X-ray structure analysis. The crystal packing is stabilized by intermolecular H-bonding and $\pi - \pi$ interactions.

Key Words: Dinuclear, intermolecular H-bonding, molybdenum, polyimines, Schiff base, tetracarbonyl.

Introduction

The coordination chemistry of pyridine, bipyridine (bipy), terpyridine (terpy), phenanthroline (phen), naphthyridine (naphthy), and pyridine-pyridazine (pyridaz) have received more and more attention since the late 19th century. Recent investigations on the unusual coordination features of these ligands were compared to classical chelating behavior to stimulate the synthesis of these complexes.¹⁻³

Schiff bases with bi- and tridentate pyridine-bis(imine) ligands have been the focus of current research in polymer science for the polymerization of ethylene and propylene.^{4,5} In our previous work, the

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catalytic properties of long-chain Schiff base complexes of molybdenum tetracarbonyl for the free radical polymerization of methyl methacrylate were described.⁶

The reaction of 2-acetylpyridine (ace) with 1,2-diamino-ethane (en) gave classical diaceen and half-unit aceen (with a free amine group) in 2:1 or 1:1 ratios, respectively. The in situ synthesis of the complexes $(\text{PPh}_4)[\text{Mo}(\text{CN})_3\text{O}(\text{aceen})]$ and $[\text{Mo}(\text{CN})_2\text{O}(\text{diaceen})]\cdot\text{H}_2\text{O}$ has been reported.⁷ The reaction of ZnX_2 (X = Cl or Br) with diaceen in THF gave $[\text{ZnX}_2(\text{diaceen})]$. However, the $[\text{ZnX}_2(\text{aceen})]$ complex was formed by either in situ or direct reaction of diaceen in hydroxylic solvent.⁸ The treatment of pyridine-2-aldehyde with 1,2-diaminoethane gave the tetradentate Schiff base ligand (L_4), which was reacted with silver(I) tetrafluoroborate to form, by self-assembly, the double stranded D_2 -helicite $(\pm)-[\text{Ag}_2(\text{L}_4)_2](\text{BF}_4)_2$.⁹ The diaceen ligand was also reacted with $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ to form a 6-coordinate $[\text{Cu}(\text{diaceen})(\text{ONO}_2)(\text{H}_2\text{O})](\text{NO}_3)$ complex. However, the reaction of 2-benzoylpyridine with 1,3-diaminopropane gave another tetradentate Schiff base ligand that was reacted with copper perchlorate in ethanol to form a distorted tetrahedral complex.^{10,11}

Coordination chemistry of these ligands with different metal to ligand ratios results in different geometries, such as tetrahedral,¹¹ square planar, pentagonal bipyramidal,¹² or octahedral^{8,10} (Figure 1, I-IV). In addition to these geometries, a variety of dimeric (Figure 1, III-IV) and oligomeric (Figure 1, V) complexes were formed.⁹ Furthermore, mononuclear 10-coordinate lanthanide(III) $[\text{M}(\text{NO}_3)_3(\text{diaceen})]$ (M = Pr or Gd) complexes were obtained by direct reaction of the tetradentate Schiff base ligand and the metal salt, independent of metal to ligand ratios.¹³

Herein, the synthesis and spectroscopic characterization of 4 tetradentate Schiff base ligands and their dinuclear molybdenum tetra-carbonyl complexes, together with the single crystal X-ray structure analysis of N,N'-bis(1-(pyridin-2-yl)ethylidene)ethane-1,2-diamine, (diaceen), are reported.

Experimental

All reactions were performed under a dry, oxygen-free nitrogen atmosphere, using solvents that were used as received from commercial sources. Micro-analyses were carried out by TÜBİTAK ATAL (Ankara Test and Analysis Laboratory) with a LECO CHNS 932. Melting points were measured on a BÜCHI B-540 melting point apparatus and are presented herein uncorrected. Atmospheric pressure chemical ionization (APCI) mass spectra were recorded with an AGILENT 1100 MSD LC-MS mass spectrometer. The ¹H-NMR spectra were recorded at room temperature in chloroform-d₁ or acetone-d₆ on a BRUKER AVANCE DPX-400 400 MHz or BRUKER/XWIN-NMR 400 MHz spectrometer operating at 400.1 MHz with SiMe₄ (0.0 ppm) as the internal reference. The quoted IR spectra were recorded on a Jasco FT-IR 300E spectrophotometer in nujol mulls between KBr pellets in the range of 4000-600 cm⁻¹. 2-Acetylpyridine, 2-benzoylpyridine, Mo(CO)₆, 1,2-diaminoethane, and 1,6-diaminohexane were used as supplied from Aldrich Chemical Company. All chemicals were of analytical reagent grade and used without further purification.

Numbering of carbon and hydrogen atoms, as in the X-ray structure of [diaceen] (**2**), was used.

Synthesis of N,N'-Bis-(phenyl-pyridin-2-yl-methylene)-ethane-1,2-diamine, [dibpen], (**1**)

2-Benzoylpyridine (3.30 mmol, 0.600 g) was added to a solution of 1,2-diaminoethane (1.30 mmol, 0.078 g) in ethanol (15 cm³) and the solution was refluxed for 4 h. After cooling to room temperature, MgSO₄ was added to remove water and the solution was filtered. The solvent was removed by rotary evaporation. Fine bright yellow crystals of compound **1** were deposited from Et₂O. The solid was washed with Et₂O and H₂O

to remove impurities and dried in vacuo. (Yield: 0.412 g, 81%); mp: 130 °C. Found: C, 79.58; H, 4.83; N, 14.04. $C_{26}H_{22}N_4$ requires: C, 79.97; H, 5.68; N, 14.35. Selected IR data (ν , cm^{-1}): 1665, 1585 (C=N). 1H -NMR ($CDCl_3$, δ ppm); 3.85 (m, 4H, C8, C9), 7.15-7.90 (m, 14H, Arom.), 8.58 (d, 2H, C2), 8.74 (d, 2H, C5) ppm. ^{13}C -NMR ($CDCl_3$, δ ppm); 169 (C6), 157 (C1), 149 (C5), 136 (C3), 124 (C4), 123 (C2), 138, 131, 128, 128 (Ph), 55 (C8, C9). APCI-MS m/z 413.2 [dibpen+Na] $^+$.

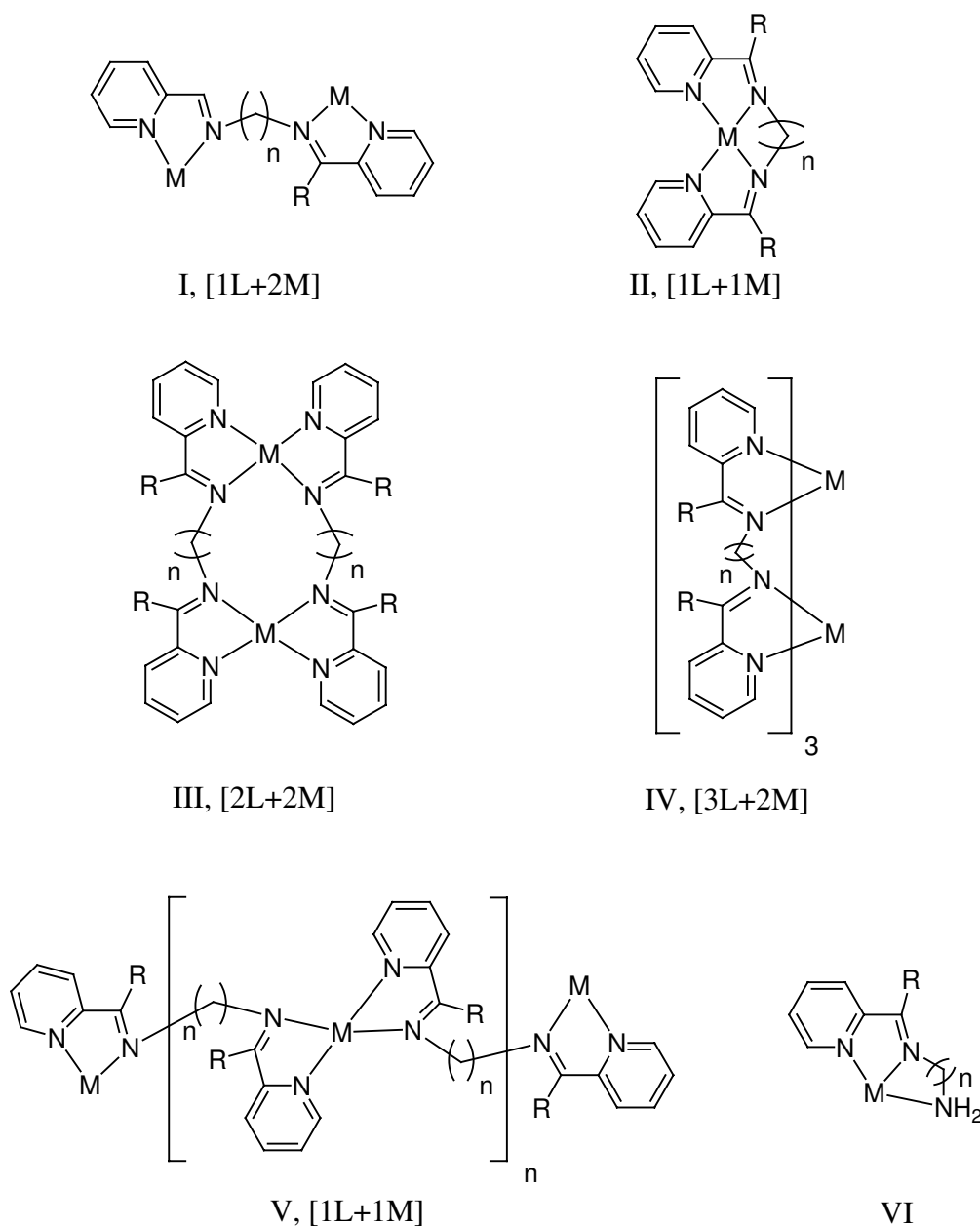


Figure 1. General structure of the metal complexes with tetradentate di-Schiff bases (I-V) and half-unit complexes (VI).

Synthesis of N,N'-Bis-(1-pyridin-2-yl-ethylidene)-ethane-1,2-diamine, [diaceen], (2)

2-Acetylpyridine (4.10 mmol, 0.500 g) and 1,2-diaminoethane (1.65 mmol, 0.100 g) similarly gave colorless crystals of compound **2**. (Yield: 0.222 g, 50%); mp: 112 °C. Found: C, 71.70; H, 7.53; N, 21.37. C₁₆H₁₈N₄ requires: C, 72.15; H, 6.81; N, 21.04. Selected IR data (ν , cm⁻¹): 1634, 1573 (C=N). ¹H-NMR (CDCl₃, δ ppm); 2.34 (s, 6H, C7), 3.88 (s, 4H, C8, C9), 7.17 (m, 2H, C4), 7.59 (m, 2H, C3), 7.97 (d, 2H, C2), 8.50 (d, 2H, C5). ¹³C-NMR (CDCl₃, δ ppm); 167 (C6), 157 (C1), 147 (C5), 135 (C3), 123 (C4), 120 (C2), 53 (C8, C9), 13 (C7). APCI-MS *m/z* 267 [diaceen]⁺.

Synthesis of N,N'-Bis-(phenyl-pyridin-2-yl-methylene)-hexane-1,6-diamine, [dibphda], (3)

2-Benzoylpyridine (4.37 mmol, 0.800 g) and 1,6-diaminohexane (2.18 mmol, 0.253 g) similarly gave the viscous compound **3**. (Yield: 0.900 g, 92%). Found: C, 74.81; H, 6.95; N, 12.38. C₃₀H₃₀N₄ 2H₂O requires: C, 74.69; H, 7.10; N, 11.61. Selected IR data (ν , cm⁻¹): 1663, 1630 (C=N). ¹H-NMR (CDCl₃, δ ppm); 1.30 (m, 4H, -CH₂-), 1.68 (m, 4H, -CH₂-), 3.33 (t, 2H, N-CH₂), 3.41 (t, 2H, N-CH₂), 7.15-8.75 (m, 18H, Arom.). ¹³C-NMR (CDCl₃, δ ppm); 167 (C6), 156 (C1), 149 (C5), 136 (C3), 124 (C4), 122 (C2), 128, 128, 130 (Ph), 58 (CH₂), 54 (CH₂), 53 (CH₂), 31 (CH₂), 27 (CH₂), 18 (CH₂). APCI-MS *m/z* 447 [dibphda]⁺.

Synthesis of N,N'-Bis-(1-pyridin-2-yl-ethylidene)-hexane-1,6-diamine, [diachda], (4)

2-Acetylpyridine (4.30 mmol, 0.520 g) and 1,6-diaminohexane (1.72 mmol, 0.200 g) similarly gave the viscous compound **4**. (Yield: 0.490 g, 88%). Found: C, 74.86; H, 8.42; N, 17.08. C₂₀H₂₆N₄ requires: C, 74.49; H, 8.13; N, 17.38. Selected IR data (ν , cm⁻¹): 1635, 1575 (C=N). ¹H-NMR (CDCl₃, δ ppm); 1.45 (m, 4H, -CH₂-), 1.72 (m, 4H, -CH₂-), 3.45 (t, 4H, N-CH₂), 2.28 (s, 6H, CH₃), 7.20 (m, 2H, C4) 7.61 (m, 2H, C3) 7.98 (d, 2H, C2), 8.50 (d, 2H, C5). ¹³C-NMR (CDCl₃, δ ppm); 166 (C6), 158 (C1), 149 (C5), 136 (C3), 123 (C4), 121 (C2), 52 (CH₂), 30 (CH₂), 31 (CH₂), 27 (CH₂), 14 (CH₃). APCI-MS *m/z* 323 [diachda]⁺.

Synthesis of [Mo₂(CO)₈(dibpen)], (1a)

To a solution of **1** (0.10 mmol, 0.040 g) in *i*-PrOH (15 mL) was added Mo(CO)₆ (0.20 mmol, 0.054 g). After refluxing under nitrogen for 4 h, the maroon solution was left to cool to room temperature. Unreacted Mo(CO)₆ was filtered off and MgSO₄ was added to the filtrate to remove water. After filtration the solvent was removed by rotary evaporation and the viscous maroon complex **1a** was obtained. (Yield: 0.064 g, 77%). Found: C, 50.28; H, 2.62; N, 6.95. C₃₄H₂₂N₄O₈Mo₂ requires: C, 50.64; H, 2.73; N, 6.95. Selected IR data (ν , cm⁻¹): 2010, 1899, 1828 (C≡O), 1663, 1578 (C=N). ¹H-NMR (CDCl₃, δ ppm); 1.17 (s, 4H, C8, C9), 7.31-8.65 (m, 18H, Arom.). ¹³C-NMR (CDCl₃, δ ppm); 154 (C6), 147 (C1), 136 (C5), 135 (C3), 125 (C4), 124 (C2), 132, 130, 127 (Ph), 28 (C8, C9), CO's not observed. APCI-MS *m/z* 803 [Mo₂(CO)₈(dibpen)]⁺.

Synthesis of [Mo₂(CO)₈(diaceen)], (2a)

In a similar manner as described for **1a**, the reaction of **2** (0.19 mmol, 0.051 g) and Mo(CO)₆ (0.38 mmol, 0.100 g) gave compound **2a** as a maroon solid. (Yield: 0.088 g, 67%); mp: >320 °C. Found: C, 42.91; H, 2.63; N, 8.63. C₂₄H₁₈N₄O₈Mo₂ requires: C, 42.25; H, 2.66; N, 8.21. Selected IR data (ν , cm⁻¹): 2005, 1896, 1840 (C≡O), 1600 (C=N). ¹H-NMR (Acetone-d₆, δ ppm); 2.80 (s, 6H, C7), 4.48 (s, 4H, C8, C9), 7.58 (m, 2H, C4), 8.08 (m, 2H, C3), 8.22 (d, 2H, C2), 9.02 (d, 2H, C5). ¹³C-NMR (Acetone-d₆, δ ppm); 171 (C6),

155 (C1), 152 (C5), 137 (C3), 126 (C4), 126 (C2), 57 (C8, C9), 15 (C7), CO's not observed. APCI-MS m/z 471 $[\text{Mo}(\text{CO})_4(\text{diaceen})]^+$.

Synthesis of $[\text{Mo}_2(\text{CO})_8(\text{dibphda})]$, (**3a**)

In a similar manner as described for **1a**, the reaction of **3** (0.22 mmol, 0.100 g) and $\text{Mo}(\text{CO})_6$ (0.45 mmol, 0.120 g) gave compound **3a** as a maroon crystalline solid. (Yield: 0.150 g, 78%); mp: 210 °C (dec.). Found: C, 52.08; H, 3.06; N, 6.55. $\text{C}_{38}\text{H}_{30}\text{N}_4\text{O}_8\text{Mo}_2$ requires: C, 52.09; H, 3.48; N, 6.50. Selected IR data (ν , cm^{-1}): 2010, 1894, 1827 (C≡O), 1588 (C=N). $^1\text{H-NMR}$ (Acetone- d_6 , δ ppm); 1.10 (m, 4H, -CH₂-), 1.85 (m, 4H, -CH₂-), 3.70 (t, 4H, N-CH₂-), 7.13 (d, 2H, C2) 7.28 (m, 4H, C4, Ph), 7.50 (m, 8H, Ph), 7.90 (m, 2H, C3), 9.05 (d, 2H, C5). $^{13}\text{C-NMR}$ (Acetone- d_6 , δ ppm); 221 (CO), 222 (CO), 203 (CO), 171 (C6), 156 (C1), 152 (C5), 137 (C3), 128 (C4), 126 (C2), 133, 130, 129, 128 (Ph), 59 (CH₂), 31 (CH₂), 26 (CH₂). APCI-MS m/z 854 $[\text{Mo}_2(\text{CO})_8(\text{dibphda})]^+$.

Synthesis of $[\text{Mo}_2(\text{CO})_8(\text{diacehda})]$, (**4a**)

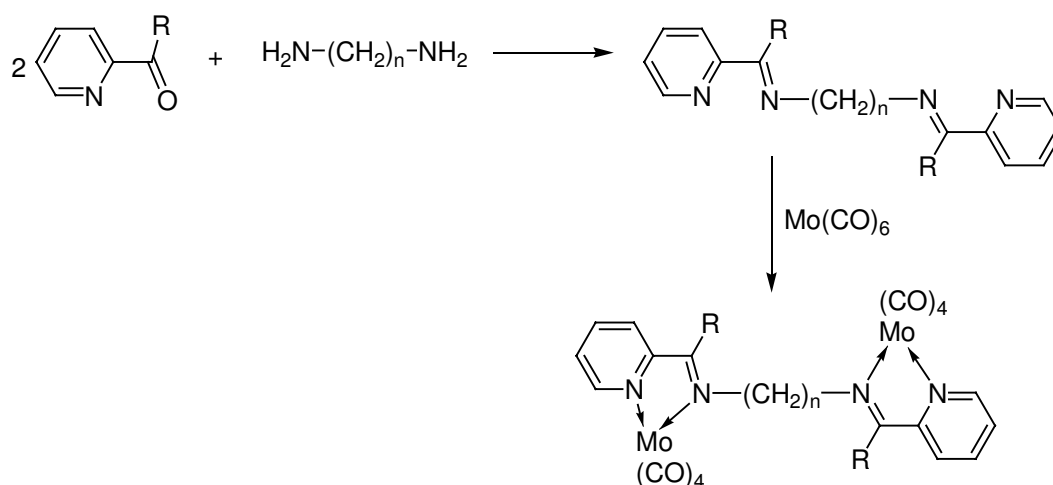
In a similar manner as described for **1a**, the reaction of **4** (0.11 mmol, 0.036 g) and $\text{Mo}(\text{CO})_6$ (0.22 mmol, 0.059 g) gave compound **4a** as a maroon solid. (Yield: 0.074 g, 90%); mp: 110 °C (dec.). Found: C, 44.42; H, 3.16; N, 7.64. $\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}_8\text{Mo}_2$ requires: C, 45.53; H, 3.52; N, 7.59. Selected IR data (ν , cm^{-1}): 2010, 1880, 1820 (C≡O), 1634 (C=N). $^1\text{H-NMR}$ (Acetone- d_6 , δ ppm); 1.50 (m, 4H, -CH₂-), 1.95 (m, 4H, -CH₂-), 2.50 (s, 6H, CH₃), 4.02 (t, 4H, N-CH₂), 7.50 (m, 2H, C4) 8.02 (m, 2H, C3) 8.10 (d, 2H, C2), 8.95 (d, 2H, C5). $^{13}\text{C-NMR}$ (CDCl_3 , δ ppm); 223 (CO), 222 (CO), 204 (CO), 169 (C6), 156 (C1), 152 (C5), 138 (C3), 126 (C4), 126 (C2), 59 (CH₂), 30 (CH₂), 27 (CH₂), 15 (CH₃). APCI-MS m/z 740 $[\text{Mo}_2(\text{CO})_8(\text{diacehda})]^+$.

Results and Discussion

Multidentate N-ligands were synthesized by the condensation reaction of 2-acetylpyridine or 2-benzoylpyridine with 1,2-diaminoethane or 1,6-diaminohexane. Dinuclear molybdenum tetracarbonyl complexes were obtained by the reactions of molybdenum hexacarbonyl with these ligands (Figure 2). The long-chain Schiff base complexes (**3a-4a**) were highly soluble, even in non-polar solvents such as petroleum ether, diethyl ether, and *n*-hexane.

The N=C stretching frequency was observed in the region 1665-1573 cm^{-1} for the ligands. These frequencies shifted to lower frequencies upon coordination to the $\text{Mo}(\text{CO})_4$ fragment. The FT-IR spectra of the *cis*-tetracarbonyl metal complexes exhibited 3 or 4 bands in the carbonyl stretching region 2010-1820 cm^{-1} . These frequencies for the complexes of unsymmetrical ligands derived from 2-acetyl- or 2-benzoylpyridine were assigned. The higher frequency A₁ and B₁ bands were assigned to the *trans*-carbonyl ligands, while the lower frequency A₁ and B₂ bands were assigned to the *cis*-carbonyls.

The results obtained from FT-IR spectra were confirmed by NMR spectral analysis. $^1\text{H-NMR}$ spectra of ligands in CDCl_3 showed the chemical shifts of the methyl groups at 2.34 and 2.28 ppm as a singlet for compounds **2** and **4**, respectively. Protons of the ethylene groups showed a multiplet or singlet at 3.85 and 3.88 ppm for compounds **1** and **2**, respectively. The protons of the hexadamine group for compound **3** showed multiplets at 1.30 (-CH₂-) and 1.68 (-CH₂-), and triplets at 3.33 (N-CH₂-) and 3.41 (N-CH₂-) ppm. Similarly, compound **4** exhibited multiplets at 1.45 (-CH₂-) and 1.72 (-CH₂-), and a triplet at 3.46 (N-CH₂-) ppm. The $^1\text{H-NMR}$ spectra of the compounds exhibited the expected peaks of aromatic protons.



<u>Compound No</u>	<u>R</u>	<u>n</u>
(1)	Ph	2
(2)	CH ₃	2
(3)	Ph	6
(4)	CH ₃	6

Figure 2. General formula and abbreviations of the tetradentate Schiff base ligand and molybdenum complexes.

¹³C-NMR spectra of the metal carbonyl complexes (**3a** and **4a**) were a strong piece of evidence suggesting that the coordination compounds formed and showed 3 signals, depending on their symmetry. The higher frequency resonance was assigned to 2 similar *trans*-carbonyls and the other peaks were assigned to *cis*-carbonyls. Other resonances were in accordance with expectations.

The LC/MS spectra were consistent with our formulations of these compounds.

The molecular structure of diaceen (**2**) is shown in Figure 3, which also gives the crystallographic numbering scheme. Details of the data collected are provided in Table 1. Selected bond lengths and angles are given in Table 2. In total, 16 molecules are contained within the unit cell of diaceen (Figure 4). The molecular interactions in diaceen are dominated by the strong intermolecular hydrogen bonds within the unit cell, indicated by the close approach of the aromatic hydrogen and imine nitrogen. It is noteworthy, in contrast to reported metal complexes of diaceen,^{7,10,13} that the intermolecular hydrogen bond within the unit cell is 2.60 Å (C4-H4...N6) (Table 3). The crystal packing is further stabilized by $\pi - \pi$ interactions between the pyridyl rings. The pyridyl rings of the molecules at (x, y, z) and (1-x, 1-y, 1-z) are stacked with the dihedral angle of 3.63(1)° and centroid-centroid separation of 4.646(2) Å, indicating $\pi - \pi$ interactions.

The C=N distance [1.271(3) Å] is similar to those found in the related compounds N,N'-bis(2-aminobenzylidene)ethane-1,2-diamine, [1.277(2) Å], N,N'-bis(5-chlorosalicylidene)ethane-1,2-diamine, [1.259(4) Å], and N,N'-bis(4-nitrobenzylidene)ethane-1,2-diamine, [1.261(2) Å].¹⁴⁻¹⁶ The C=N distance is also similar to those found in the metal complexes [Mo(CN)₂O(diaceen)].H₂O [1.280(3) and 1.292(4) Å], [ZnCl₂(aceen)]

[1.267(6) Å], and [Cu(diaecen)(ONO₂)(H₂O)](NO₃) [1.260(6) Å].^{7,8,10} The bond angles of the imine nitrogen atoms N2 and N3 are 118.2(2) and 119.6(2)°, respectively, which confirm their sp² characters.

Table 1. Crystallographic data and parameters of diaecen (**2**).

Formula	C ₁₆ H ₁₈ N ₄
Mol. Wt.	266.34
Color/shape	Colorless/ prism
Crystal system	Orthorhombic
Space group	Pbca
a/ Å	12.2947(5)
b/ Å	24.6051(10)
c/ Å	19.4317(11)
α/°	90
β/°	90
γ/°	90
V/ Å ³	5878.3(5)
Z	16
D _(calc.) / Mg m ⁻³	1.204
μ/ mm ⁻¹	0.074
F(000)	2272
Cell refinement (reflections)	32746
Crystal size/ mm	0.34 × 0.50 × 0.62
Scan range θ °	26.06
Scan index limits (h/k/l)	15, -15; 30, -30; 23, -23
Abs. correction T min, max	0.9637, 0.9832
Data collected	56683
Unique data	5800
Goodness of fit on F ²	0.881
a, b ^a in weighting scheme	0.080, 0.000
R(int)	0.105
Observed data [F > 4σ(F)]	2710
parameters n	361
Δρ e Å ⁻³	0.219, -0.169
Final R indices [I > 2σ(I)]	R1 = 0.0544, wR2 = 0.1616

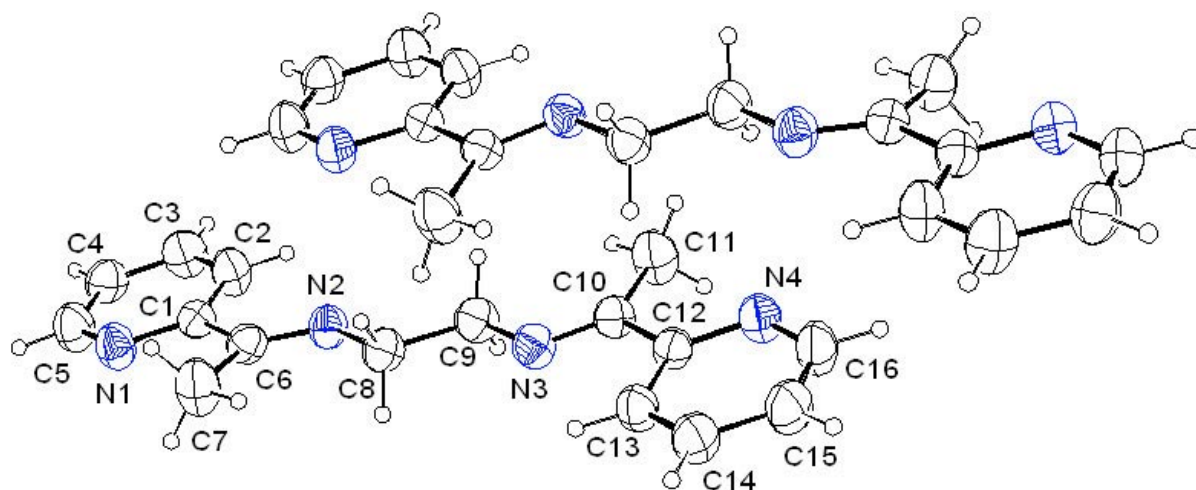


Figure 3. The molecular structure of **2** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

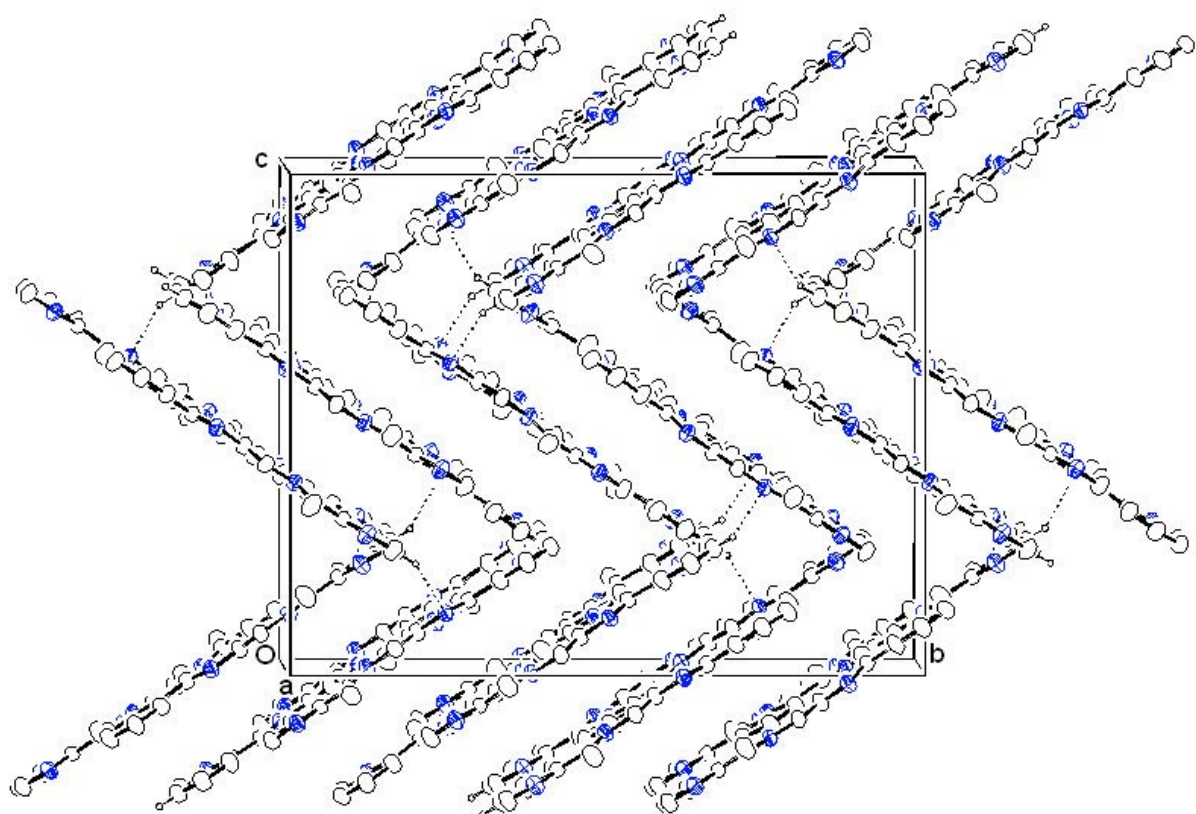


Figure 4. A packing diagram for **2**. Hydrogen bonds are shown as dashed lines.

Table 2. Selected bond lengths (Å) and angles (°) for diaceen (**2**).

C1-N1	1.330(3)
C6-N2	1.271(3)
C8-N2	1.466(3)
C9-N3	1.468(3)
C8-C9	1.507(3)
C2-C3	1.382(4)
N2-C6-C1	116.5(2)
N2-C6-C7	125.8(2)
N2-C8-C9	109.79(19)
N3-C9-C8	107.86(19)

Table 3. Hydrogen-bonding geometry (Å) for diaceen (**2**).

D—H...A	D—H	H...A	D...A	D—H...A
C4—H4...N6 ⁱ	0.93	2.60	3.469 (3)	155.2

Symmetry codes: (i) 1 - x, y - 1/ 2, 3/2 - z.

Multidentate Schiff base ligands can form different types of complexes, depending on the metal center (Figure 1). We were interested in preparing coordination and organometallic polymers with tetradentate Schiff base ligands. It was found that the reactions of the tetradentate Schiff base ligands with Mo(CO)₆ gave dinuclear complexes.

X-ray data collection and cell refinement were achieved with X-Area. The data reduction was performed by X-RED32. SHELXS97 was used to solve the structure and SHELXL97 was used to refine the structure. Molecular graphics were prepared using WinGX. DIAMOND was used to prepare the material for publication.^{17–22}

Supplementary material

Crystallographic data for the structural analysis are deposited at the Cambridge Crystallographic Data Centre, CCDC no. 638238 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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