

Note

Synthesis and X-ray structures of some Group 6 metal carbonyl bis(2-pyridyl)formamidine complexes

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Abstract

New complexes of the types $M(\text{CO})_4(\text{HDpyF})$ ($M = \text{Cr}$, **1**; $M = \text{W}$, **2**) and $\text{Mo}(\text{CO})_3(\text{HDpyF})(\text{CH}_3\text{CN})$ (**3**), have been prepared by the reactions of bis(2-pyridyl)formamidine (HDpyF) with corresponding Group 6 metal hexacarbonyls in THF and CH_3CN , respectively. The HDpyF ligands in complexes **1–3** coordinate to the metal centers in novel bidentate fashions but in different bonding modes. All the three complexes show supramolecular structures in the solid state by intermolecular hydrogen bonding and aromatic π – π stacking interactions. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The anion of the ligand bis(2-pyridyl)formamidine, DpyF^- , has been subjected to several studies of its coordination ability to metal centers. Tridentate and tetradentate coordination modes **I–III** (Scheme 1) were seen for this ligand. In the tetradentate mode of coordination, **I**, the four nitrogen atoms are in a linear array for coordination to the metals. Such coordination was found in the tetranuclear complex $[\text{Cr}_4(\text{DpyF})_4\text{Cl}_2]\text{Cl}_2$ [**1**]. The nitrogen atoms of the DpyF^- ligands in the trinuclear complexes of $[\text{Cr}_3(\text{DpyF})_4][\text{PF}_6]_2$ are also in a linear array, **II**, but one of the terminal nitrogen atoms is not coordinated [**1**]. A third coordination mode, **III**, which features chelation by two nitrogen atoms together with the formation of a bridge by the other two nitrogen atoms, was found in the three isomorphous linear trinuclear complexes $[\text{M}_3(\text{DpyF})_4][\text{PF}_6]_2$ ($M = \text{Cu}$, Co and Fe) [**2**]. No complex containing neutral

HDpyF ligand has been reported. We report herein the first mononuclear complexes of HDpyF ligands that coordinate to the metal centers in bidentate, **IV** and **V**, fashion, respectively. The synthesis and structures of $M(\text{CO})_4(\text{HDpyF})$ ($M = \text{Cr}$, W) and $\text{Mo}(\text{CO})_3(\text{HDpyF})(\text{CH}_3\text{CN})$ form the subject of this report.

2. Experimental

2.1. General procedures

All manipulations were carried out under dry, oxygen-free nitrogen by using Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. *n*-Hexane and THF were purified by distillation from sodium–benzophenone, and acetonitrile and dichloromethane from P_2O_5 . The visible absorption spectra were recorded on a Hitachi U-2000 spectrophotometer. The IR spectra were recorded on a Bio-Rad FTs-7 spectrometer.

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2.2. Materials

The complexes $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}$ and W) were purchased from Strem Chem. Co. and the ligand bis(2-pyridyl)formamidine was prepared according to previously reported procedures [3].

2.3. Preparations

2.3.1. $\text{Cr}(\text{CO})_4(\text{HDpyF})$

$\text{Cr}(\text{CO})_6$ (0.047 g, 0.20 mmol) and HDpyF (0.04 g, 0.20 mmol) were placed in a flask containing 10 ml of THF. The mixture was then refluxed for 3 h to yield an orange solution. The solvent was reduced and *n*-hexane added to induce precipitation. The solid was filtered, washed with ether and then dried under reduced pressure. Yield: 0.049 g (67%). UV-vis (CH_2Cl_2 ; λ_{max}): 479 nm ($\epsilon = 142 \text{ M}^{-1} \text{ cm}^{-1}$). Anal. Found: C, 49.32; H, 2.48; N, 15.69. Calc. for $\text{C}_{15}\text{H}_{10}\text{CrN}_4\text{O}_4$ (MW = 362.27): C, 49.73; H, 2.78; N, 15.41%. IR (cm^{-1} , KBr disk): ν 3370br (NH), 2010m (CO), 1895m (CO), 1874m (CO), 1796m (CO).

2.3.2. $\text{W}(\text{CO})_4(\text{HDpyF})$

$\text{W}(\text{CO})_6$ (0.35 g, 1.0 mmol) and HDpyF (0.20 g, 1.0 mmol) were placed in a flask containing 15 ml of THF. The mixture was then refluxed for 3 h to yield a brown solution. The solvent was reduced and *n*-hexane added to induce precipitation. The solid was filtered, washed with ether and then dried under reduced pressure. Yield: 0.27 g (55%). UV-vis (CH_2Cl_2 ; λ_{max}): 466 nm

($\epsilon = 844 \text{ M}^{-1} \text{ cm}^{-1}$). Anal. Found: C, 36.77; H, 2.01; N, 11.40. Calc. for $\text{C}_{15}\text{H}_{10}\text{WN}_4\text{O}_4$ (MW = 494.12): C, 36.46; H, 2.04; N, 11.34%. IR (cm^{-1} , KBr disk): ν 3341br (NH), 2018 m (CO), 1921m (CO), 1872m (CO), 1797m (CO).

2.3.3. $\text{Mo}(\text{CO})_3(\text{HDpyF})(\text{CH}_3\text{CN})$

$\text{Mo}(\text{CO})_6$ (0.52 g, 2.0 mmol) and HDpyF (0.41 g, 2.0 mmol) were placed in a flask containing 10 ml of CH_3CN . The mixture was then refluxed for 3 h to yield an orange solution. The solvent was reduced and *n*-hexane added to induce precipitation. The solid was filtered, washed with ether and then dried under reduced pressure. Yield: 0.35 g (42%). UV-vis (CH_2Cl_2 ; λ_{max}): 456 nm ($\epsilon = 607 \text{ M}^{-1} \text{ cm}^{-1}$). Anal. Found: C, 45.80; H, 3.44; N, 16.22. Calc. for $\text{C}_{16}\text{H}_{13}\text{MoN}_5\text{O}_3$ (MW = 419.01): C, 45.84; H, 3.13; N, 16.70%. IR (cm^{-1} , KBr disk): ν 3313br (NH), 1901m (CO), 1789m (CO), 1724m (CO).

2.4. X-ray crystallography

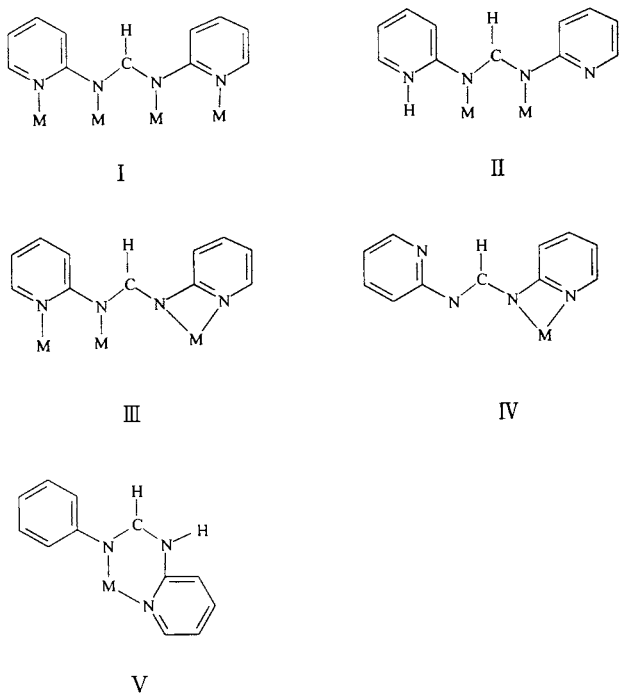
2.4.1. $\text{Cr}(\text{CO})_4(\text{HDpyF})$

Crystals suitable for X-ray diffraction were obtained by the slow diffusion of ether into a CH_2Cl_2 solution of $\text{Cr}(\text{CO})_4(\text{HDpyF})$. The diffraction data of $\text{Cr}(\text{CO})_4(\text{HDpyF})$ was collected on a Siemens CCD diffractometer, which was equipped with graphite-monochromated $\text{Mo-K}\alpha$ ($\lambda_\alpha = 0.71073 \text{ \AA}$) radiation. Data reduction was carried out by standard methods with the use of well-established computational procedures [4]. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1.

A brown crystal of $\text{Cr}(\text{CO})_4(\text{HDpyF})$ was mounted on the top of a glass fiber with epoxy cement. The hemisphere data-collection method was used to scan the data points at $2\theta < 50^\circ$. The structure factors were obtained after Lorentz and polarization corrections. The positions of the heavy atoms, including two molybdenum atoms, were located by the direct method. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements [5]. The final residuals were $R_1 = 0.0698$, $wR_2 = 0.1713$.

2.4.2. $\text{W}(\text{CO})_4(\text{HDpyF})$ and $\text{Mo}(\text{CO})_3(\text{HDpyF})(\text{CH}_3\text{CN})$

The X-ray procedures for $\text{W}(\text{CO})_4(\text{HDpyF})$ and $\text{Mo}(\text{CO})_3(\text{HDpyF})(\text{CH}_3\text{CN})$ were similar to those for $\text{Cr}(\text{CO})_4(\text{HDpyF})$. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1. Some selected bond distances and angles for $M(\text{CO})_4(\text{HDpyF})$ ($M = \text{Cr}, \text{W}$) and $\text{Mo}(\text{CO})_3(\text{HDpyF})(\text{CH}_3\text{CN})$ are listed in Tables 2 and 3, respectively.



Scheme 1. Bonding modes of DpyF⁻ ligand that have been reported.

Table 1
Crystal data for Cr(CO)₄(HDpyF) (**1**), W(CO)₄(HDpyF) (**2**), and Mo(CO)₃(HDpyF)(CH₃CN) (**3**)

	1	2	3
Formula	C ₁₅ H ₁₀ CrN ₄ O ₄	C ₁₅ H ₁₀ WN ₄ O ₄	C ₁₆ H ₁₃ MoN ₅ O ₃
Formula weight	362.27	494.12	419.25
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	7.339(1)	7.319(1)	15.826(1)
<i>b</i> (Å)	9.618(1)	9.788(1)	7.760(1)
<i>c</i> (Å)	12.062(1)	12.094(1)	15.313(1)
α (°)	80.022(2)	79.901(1)	90
β (°)	79.867(2)	79.243(1)	115.712(2)
γ (°)	69.883(2)	69.497(1)	90
<i>V</i> (Å ³)	781.1(1)	791.5(1)	1694.4(3)
<i>Z</i>	2	2	4
μ (Mo–K α) (mm ⁻¹)	0.760	7.324	0.800
Temperature (°C)	25	25	25
Independent reflections	2637 [<i>R</i> _{int} = 0.0535]	2766 [<i>R</i> _{int} = 0.0350]	2782 [<i>R</i> _{int} = 0.0302]
Data/restraints/parameters	2637/0/253	2766/0/257	2782/0/279
Quality-of-fit indicator ^a	1.098	1.152	1.130
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^{b,c}	<i>R</i> ₁ = 0.0698, <i>wR</i> ₂ = 0.1713	<i>R</i> ₁ = 0.0243, <i>wR</i> ₂ = 0.0648	<i>R</i> ₁ = 0.0371, <i>wR</i> ₂ = 0.0992
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0828, <i>wR</i> ₂ = 0.1851	<i>R</i> ₁ = 0.0246, <i>wR</i> ₂ = 0.0650	<i>R</i> ₁ = 0.0422, <i>wR</i> ₂ = 0.1068

^a Quality-of-fit = $[\sum w(|F_o^2| - |F_c^2|)^2 / (N_{\text{observed}} - N_{\text{parameters}})]^{1/2}$.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^c $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (ap)^2 + (bp)]$, where $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$; and $a = 0.1005$, $b = 0.7703$ for **1**; $a = 0.0293$, $b = 1.5698$ for **2**; and $a = 0.0511$, $b = 1.9538$ for **3**.

3. Results and discussion

3.1. Syntheses and spectroscopic studies

Reaction of M(CO)₆ (M = Cr, W) with HDpyF in refluxing THF afforded the complex M(CO)₄(HDpyF) (M = Cr, **1**; M = W, **2**). When Mo(CO)₆ was reacted with HDpyF in refluxing CH₃CN, complex of the type Mo(CO)₃(HDpyF)(CH₃CN), **3**, was prepared. The reaction pathways are shown in Scheme 2. These complexes are stable as solids but slowly decompose in solution. Four and three ν (CO) vibrations were observed in the solid infrared spectra for the complexes [M(CO)₄(HDpyF)] (M = Cr, W) and [Mo(CO)₃(HDpyF)](CH₃CN), respectively, as expected for the octahedral complex with C₁ symmetry.

3.2. Structures

Fig. 1 shows a representative ORTEP diagram for **1** and **2**. Complexes **1** and **2** are isostructural and the metal atoms adopt a distorted octahedron and coordinated to four COs and one HDpyF ligand. It is seen that the HDpyF ligand chelates the metal atom through the first and the second nitrogen atoms to form a four-membered ring, and the third and the fourth nitrogen atoms are not coordinated. Due to the formation of the four-membered ring, the N(1)–Cr–N(2) angle is 61.6(2)° and N(1)–Cr–C(3) and N(2)–Cr–C(4) are

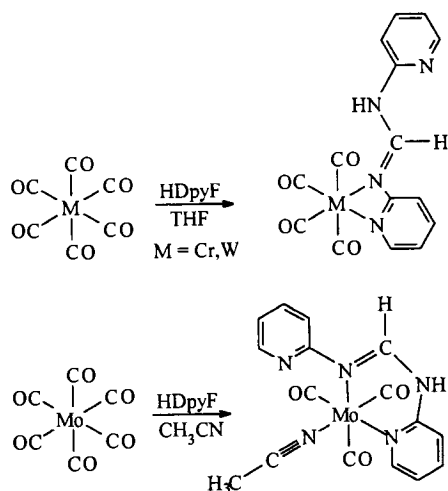
104.6(2) and 104.8(2)°, respectively. A similar situation is also observed for complex **2**. The N(1)–W–N(2) angle is 58.1(2)° and N(1)–W–C(3) and N(2)–W–C(4)

Table 2
Selected bond distances (Å) and angles (°) for M(CO)₄(HDpyF)

	M=Cr	M=W
<i>Bond distances</i>		
M–C(1)	1.894(6)	2.036(6)
M–C(2)	1.894(5)	2.029(6)
M–C(3)	1.829(5)	1.937(5)
M–C(4)	1.825(6)	1.943(6)
M–N(1)	2.145(4)	2.269(4)
M–N(2)	2.141(4)	2.251(4)
<i>Bond angles</i>		
C(1)–M–N(1)	91.4(2)	93.2(2)
C(1)–M–N(2)	91.5(2)	94.3(2)
C(2)–M–C(1)	174.3(2)	175.1(2)
C(2)–M–N(1)	93.5(2)	91.0(2)
C(2)–M–N(2)	93.4(2)	90.1(2)
C(3)–M–C(1)	88.1(2)	87.2(2)
C(3)–M–C(2)	87.8(2)	89.0(2)
C(3)–M–N(1)	104.6(2)	107.8(2)
C(3)–M–N(2)	166.1(2)	165.9(2)
C(4)–M–C(3)	89.0(2)	87.8(3)
C(4)–M–N(1)	166.4(2)	164.4(2)
C(4)–M–N(2)	104.8(2)	106.3(2)
C(4)–M–C(1)	88.7(2)	87.5(2)
C(4)–M–C(2)	87.3(2)	89.2(3)
N(2)–M–N(1)	61.6(2)	58.1(2)

Table 3
Selected bond distances (Å) and angles (°) for Mo(CO)₃-(HDpyF)(CH₃CN)

Bond distances			
Mo–C(1)	1.926(4)	Mo–C(2)	1.930(4)
Mo–C(3)	1.933(5)	Mo–N(5)	2.255(3)
Mo–N(2)	2.274(3)	Mo–N(4)	2.292(3)
Bond angles			
C(1)–Mo–C(2)	84.8(2)	C(1)–Mo–C(3)	83.6(2)
C(2)–Mo–C(3)	89.2(2)	C(1)–Mo–N(5)	97.38(14)
C(2)–Mo–N(5)	177.06(14)	C(3)–Mo–N(5)	93.0(2)
C(1)–Mo–N(2)	178.05(12)	C(2)–Mo–N(2)	96.99(13)
C(3)–Mo–N(2)	97.0(2)	N(5)–Mo–N(2)	80.76(10)
C(1)–Mo–N(4)	98.93(14)	C(2)–Mo–N(4)	94.47(14)
C(3)–Mo–N(4)	175.7(2)	N(5)–Mo–N(4)	83.31(11)
N(2)–Mo–N(4)	80.31(11)		



Scheme 2. Reaction pathways for M(CO)₄(HDpyF) and Mo(CO)₃(HDpyF)(CH₃CN).

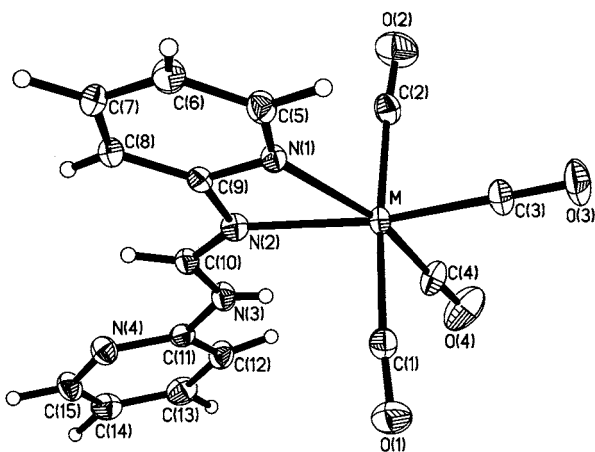


Fig. 1. Representative ORTEP drawing of M(CO)₄(HDpyF) (M = Cr, 1; M = W, 2).

are 107.8(2) and 106.3(2)°, respectively. It is also interesting to note that the M–C distance *trans* to the carbonyl group is longer than those *trans* to the ni-

trogen atoms of the HDpyF ligand. The differences are about 0.07 Å for **1** and 0.09 Å for **2**, respectively. Since the uncoordinated pyridine ring are free to rotate about the C–N bond to the bonded nitrogen atom, both the *ortho* positions of the uncoordinated ring, i.e. C(12) and N(4) are possible positions for the nitrogen atom before the structure was determined. These two conformations were assumed and the structures refined. The structure shown in Fig. 1 is the best fit to the refinement result. The conformation of HDpyF ligand in Fig. 1 is also the one found directly from the electron density map, i.e. by identifying the position of the hydrogen atom. This conformation is depicted as **IV** in Scheme 1. As seen in Fig. 1, the two *trans* carbonyl groups are obviously bent away from the ligand pyridyl rings, with M–C–O angles of 175.7(5) and 173.8(5)° for **1** and 174.6(5) and 175.8(6)° for **2**, respectively. This may be ascribed to the crowding effect of the HDpyF ligand. The bidentate HDpyF ligand in each molecule is not flat, but twisted around the C–N bonds, with dihedral angles between the planes of the two pyridine rings of 19.8° in **1** and 21.4° in **2**, respectively.

Self-assembly of the molecules in the crystal through intermolecular hydrogen bonding and/or π–π stacking interactions has been the subject of intensive study in crystal engineering [6]. Several types of hydrogen bondings and π–π stacking interactions were observed in the crystal lattices of complexes **1** and **2**. The crystal packing for complexes **1** and **2** (Fig. 2) shows that the molecules are linked into a two-dimensional molecular sheet via extensive intermolecular hydrogen bonding interactions between the C–H groups of the pyridine rings and the oxygen atoms in the adjacent molecules (H···O = 2.448 Å, ∠C–H···O = 160.4° and H···O = 2.557 Å, ∠C–H···O = 135.2° for **1**; H···O = 2.355 Å, ∠C–H···O = 157.2° and H···O = 2.569 Å, ∠C–H···O = 132.1° for **2**). The molecular sheets are further linked to each other through aromatic π–π stacking interactions to form an infinite three-dimensional network. The interplanar distances between the pyridyl rings are 3.82 and 4.04 Å for **1** and 3.82 and 4.06 Å for **2**, respectively.

Fig. 3 shows a representative ORTEP diagram for **3**. It is seen that three carbonyl groups, one acetonitrile ligand and one HDpyF ligands coordinate to the Mo center. The three carbonyl groups are located in a *fac* position. The HDpyF ligand chelates to the Mo center through the first and the third nitrogen atoms to form a six-membered ring, leaving the second and the fourth nitrogen atoms not coordinated. The conformation is depicted as **V** in Scheme 1. The N(2)–Mo–N(4) angle is 80.31(11)° and N(4)–Mo–N(5) and N(2)–Mo–N(5) are 83.31(11) and 80.76(10)°, respectively. The three Mo–C distances *trans* to the

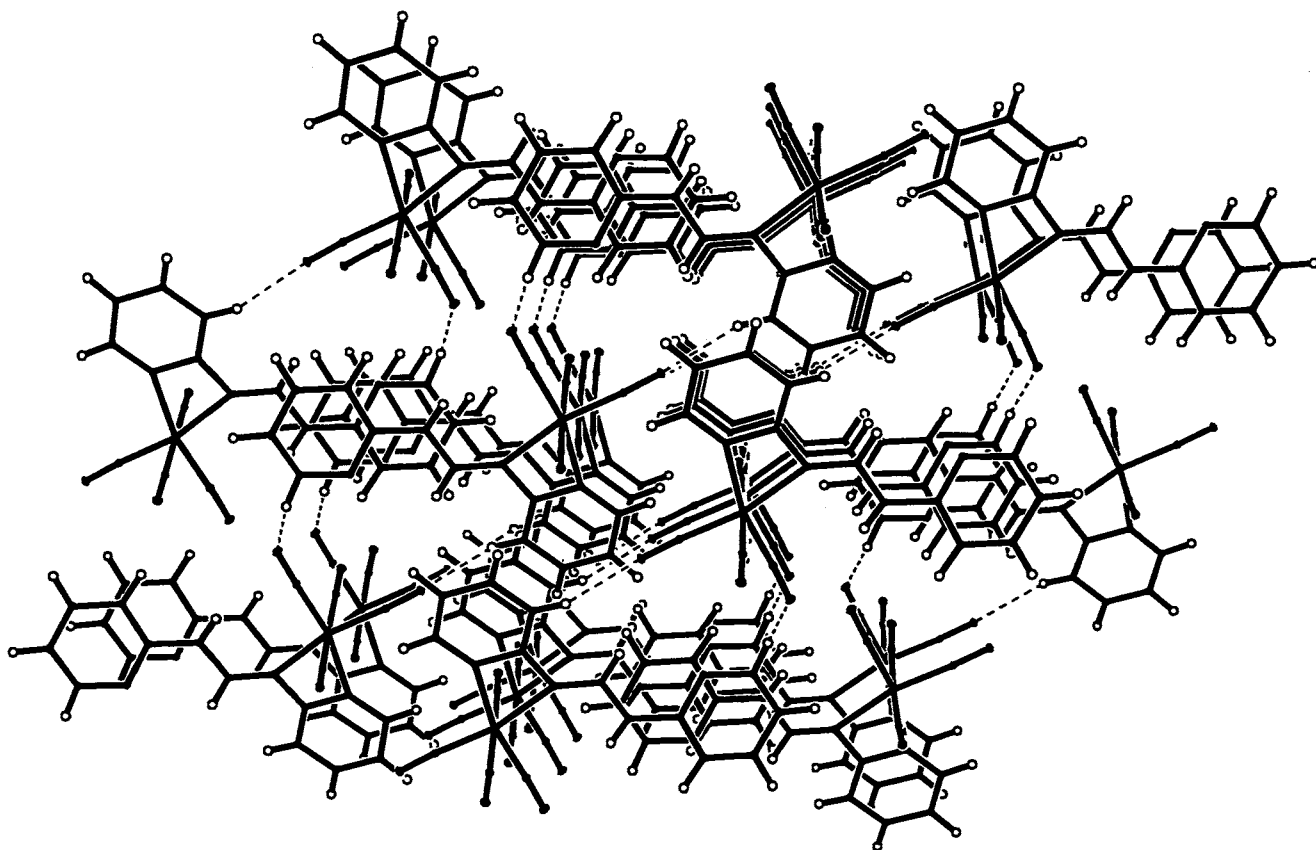


Fig. 2. Crystal packing diagram for $M(CO)_4(HDpyF)$.

nitrogen atoms are similar but the Mo–N(4) distance is the longest among the three Mo–N distances. The position of the fourth nitrogen atom was directly located from the electron density map by identifying the positions of the hydrogen atoms. The bidentate HDpyF ligand in the molecule is not flat, but twisted around the C–N bonds, with a dihedral angle between the planes of the two pyridine rings of 44.2° . This dihedral angle is quite larger than those for **1** and **2**. The crystal packing (Fig. 4) of **3** also shows that the molecules are associated with each other by extensive intermolecular hydrogen-bonding interactions, leading to an infinite two-dimensional molecular sheet. One of the hydrogen bonds involves the interaction between the hydrogen atom of the acetonitrile ligand and the oxygen atom in an adjacent molecule ($H\cdots O = 2.554 \text{ \AA}$, $\angle C-H\cdots O = 171.5^\circ$) and the other one between the hydrogen atom of the uncoordinated NH group and the oxygen atom ($H\cdots O = 2.127 \text{ \AA}$, $\angle N-H\cdots O = 169.5^\circ$). The molecular sheets are further linked through one set of aromatic π – π stacking interaction with the interplanar distance between the pyridyl rings of 3.92 \AA . The reason why only the pyridine rings coordinated to the Mo centers form π – π stacking interactions is possibly due to the large dihedral angle (44.2°) between the two pyridine rings.

4. Conclusions

The synthesis and structures of three new species $Cr(CO)_4(HDpyF)$, $Mo(CO)_3(HDpyF)(CH_3CN)$ and $W(CO)_4(HDpyF)$ have been successfully accomplished. All the three complexes show supramolecular structures in the solid state by intermolecular hydrogen bonding and aromatic π – π stacking interactions. They are the first examples of the HDpyF ligands that coordinate to

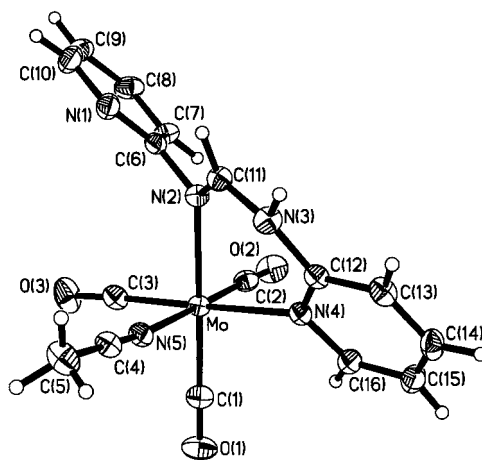


Fig. 3. ORTEP drawing of $Mo(CO)_3(HDpyF)(CH_3CN)$.

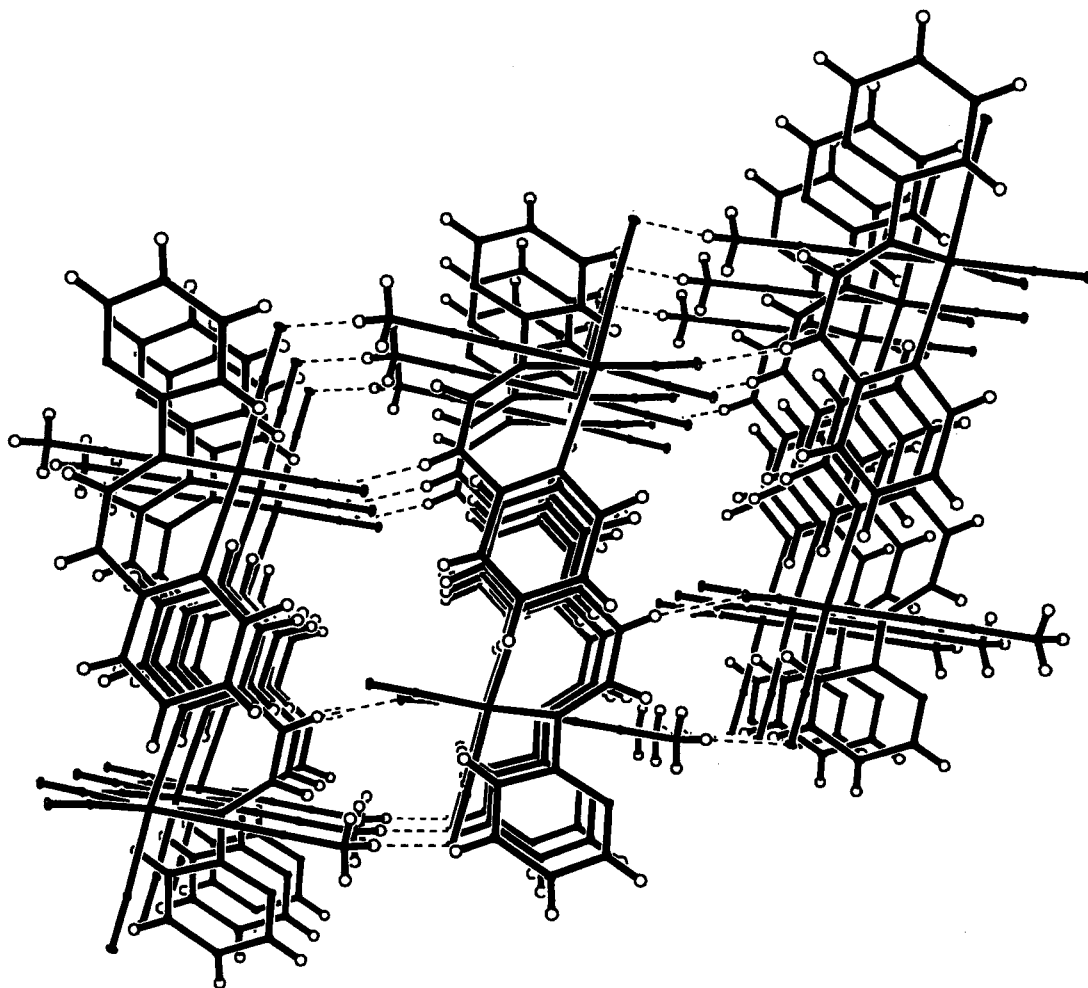


Fig. 4. Crystal packing diagram for $\text{Mo}(\text{CO})_5(\text{HDpyF})(\text{CH}_3\text{CN})$.

the mononuclear metal centers in unique bidentate fashion. It is also shown that replacement of a carbonyl group by the acetonitrile ligand has resulted in a drastic change of the bonding mode of the HDpyF ligand.

5. Supplementary material

Crystallographic data (CIF files) for the structures 1–3 have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 133942. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Also, copies of tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters and H-atoms coordinates for complexes 1, 2 and 3 (19 pages) and three listings of observed and calculated

structural factors (20 pages) are available from author J.D.C. upon request.

Acknowledgements

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