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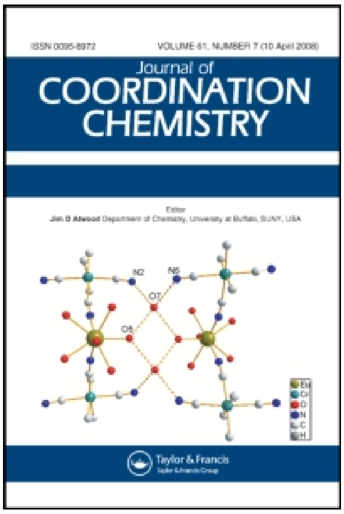

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Synthesis of 2,2′-bipyrimidine platinum(II) complexes

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Multinuclear Pt(II) complexes of 2,2′-bipyrimidine (bipm) were prepared and characterized by elemental analyses and standard spectroscopic techniques. The complexes were formulated as $[Pt(bipm)_2][PtCl_4]PhCN$ (**1**), $[Pt_3(\mu\text{-bipm})_2(bipm)_2]Cl_6$ (**2**), $[Pt_2(\mu\text{-bipm})(bpy)Cl_2]Cl_2$ (**3**), $[Pt_3(\mu\text{-bipm})_2(biq)_2]Cl_6 \cdot Me_2CO \cdot MeCN$ (**4**), $[Pt_3(\mu\text{-bipm})_2(dmg)_2]Cl_2 \cdot MeCN$ (**5**) and $[Pt_5(\mu\text{-bipm})_2(dmg)_2]Cl_8 \cdot 2PhCN$ (**6**), $[Pt_3(\mu\text{-bipm})_2(bpy)_2]Cl_6 \cdot 2Me_2CO \cdot 6PhCN$ (**7**), $[Pt_4(\mu\text{-bipm})_3(phen)_2]Cl_8 \cdot 8PhCN$ (**8**), $[Pt_4(\mu\text{-bipm})_3(ox)_2]Cl_4 \cdot H_2O \cdot 2PhCN$ (**9**); (bpy = 2,2′-bipyridine; dmg = dimethylglyoxime; ox = oxalate; phen = 1,10-phenanthroline; biq = 2,2′-biquinoline).

Keywords: Synthesis; Bipyrimidine; Multinuclear Pt(II) complexes

1. Introduction

Multinuclear complexes in which the metal centers interact through ligand bridges have potential applications in such diverse areas as catalysis, materials, medicine and sensor technology [1]. Variation of the metal centers or ligands can lead to a tailoring of the spectroscopic and redox properties.

Recent studies have been directed toward aromatic bridging ligands such as 2,2′-bipyrimidine (hereafter denoted bipm; figure 1) [2] to be used in the construction of polymetallic complexes [1, 3–7]. Bipm can coordinate as bidentate chelating or as bis-bidentate bridging ligands [8, 9] and therefore impart interesting and useful spectroscopic and redox properties on polymetallic complexes.

Furthermore, platinum(II) complexes of α-diimine ligands such as 2,2′-bipyridine (bpy) or 2,2′-bipyrimidine (bipm) and related compounds have received increasing attention because of special features such as photophysical behavior [10–20], chemical or electrochemical reduction behavior, physiological behavior inside cells and toward the DNA in continuing efforts for the advancement of metal-based tumor

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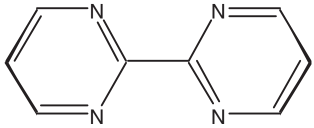

Figure 1. Bipyrimidine structure.

therapy [8, 21–23] and their potential use as catalysts and catalyst precursors for C–H bond activation [8, 22–25].

Thus we undertook this study of the synthesis and characterization of several multinuclear platinum(II) complexes containing bipm ligand as the bridging ligand with other terminal ligands.

2. Experimental

2.1. *Materials*

All materials were purchased from Aldrich and were used as received. The Pt precursor complex $[Pt(PhCN)_2Cl_2]$ (hereafter denoted complex **A**), was obtained following literature procedure [26].

2.2. *Physical measurements*

Melting points were determined on an electrothermal melting point apparatus (Electrothermal 9001), IR spectra were recorded on a Nicolet FT-IR spectrophotometer using KBr discs. Far IR spectra were analyzed on a Perkin Elmer spectrophotometer model 2000 using CsI discs. Conductivity measurements were carried out on a Conductivity Meter LF 538 at 25°C for 10^{-3} M solutions in DMF and DMSO. UV-vis spectra were recorded on a Unicam u.v.-vis spectrometer for 10^{-5} M solutions in DMF. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker MAX 300 MHz spectrometer, in DMSO and DMF as solvents using Me_4Si as internal standard. Elemental analyses for C, H and N were carried out on a Perkin-Elmer analyzer 2400 in the Central Unit Laboratories, Al al-Bayt University, Jordan.

2.3. *Synthesis*

2.3.1. $[Pt(bipm)_2][PtCl_4]PhCN$ (1). To a solution of complex **A** (1.0 mmol; 0.47 g) in 1 : 2 EtOH–Me_2CO (30 mL), bipm (1.0 mmol; 0.16 g) in 10 mL Me_2CO was added. The reaction was refluxed for 5 h, whereupon orange-red precipitate was formed. The solid was removed by filtration, washed with 1 : 1 Me_2CO–EtOH and then with Et_2O and dried *in vacuo*.

2.3.2. $[Pt_3(\mu\text{-bipm})_2(bipm)_2]Cl_6$ (2). A solution of bipm (1.0 mmol; 0.16 g) in Me_2CO (15 mL) was added to a solution of complex **A** (2.0 mmol; 0.95 g) dissolved in 15 mL MeCN. The mixture refluxed for 5 h, whereupon red-brown solid precipitated. The product was filtered off and washed with Me_2CO and then with Et_2O and dried under vacuum.

2.3.3. $[Pt_2(\mu\text{-bipm})(bpy)Cl_2]Cl_2$ (3). To complex **A** (0.50 mmol; 0.23 g) dissolved in Me_2CO (15 mL), bipm (0.25 mmol; 0.040 g) in 5.0 mL Me_2CO was added. The reaction mixture was stirred for 10 min and then bpy (0.50 mmol; 0.080 g) in 5.0 mL Me_2CO was added. The mixture was refluxed for 2 h, and left undisturbed for 48 h, whereupon a deep red precipitate was obtained. This was filtered, washed with small portions of Me_2CO and Et_2O, and dried under vacuum.

2.3.4. $[Pt_3(\mu\text{-bipm})_2(biq)_2]Cl_6 \cdot Me_2CO \cdot MeCN$ (4). To 1.0 mmol (0.47 g) of complex **A** dissolved in 1 : 1.5 MeCN–Me_2CO (25 mL), bipm (0.50 mmol; 0.080 g) in 10 mL Me_2CO was added. The reaction mixture was stirred for 10 min and then biq (1.0 mmol; 0.26 g) in 1 : 3 Me_2CO–MeCN (20 mL) was added. The reaction was refluxed for 6 h, whereupon orange-red precipitate was formed. The solid was then filtered, washed well with Me_2CO and Et_2O and dried under vacuum.

2.3.5. $[Pt_3(\mu\text{-bipm})_2(dmg)_2]Cl_2 \cdot MeCN$ (5) and $[Pt_5(\mu\text{-bipm})_2(dmg)_2]Cl_8 \cdot 2PhCN$ (6). A solution of bipm (0.50 mmol; 0.080 g) in MeCN (10 mL) was added to complex **A** (1.0 mmol; 0.47 g) in MeCN (10 mL) and the mixture was stirred for 10 min. To the resulting mixture dmg (1.0 mmol; 0.11 g) was added and the mixture refluxed for 3 h. The resulting dark green precipitate (**5**) was removed by filtration, washed with Me_2CO and Et_2O and dried *in vacuo*. The resulting filtrate, stored for three days, gave dark red precipitate (**6**). The solid was then filtered, washed well with Me_2CO and Et_2O and dried under vacuum.

2.3.6. $[Pt_3(\mu\text{-bipm})_2(bpy)_2]Cl_6 \cdot 2Me_2CO \cdot 6PhCN$ (7). To complex **A** (1.0 mmol; 0.47 g) in 40 mL Me_2CO, 1.0 mmol of bpy and 0.50 mmol bipm in 20 mL Me_2CO were added. The reaction mixture was refluxed for 1 h. Upon standing undisturbed for three days, an orange solid precipitated and was filtered off. The product was washed with Me_2CO and then with Et_2O and dried under vacuum.

2.3.7. $[Pt_4(\mu\text{-bipm})_3(phen)_2]Cl_8 \cdot 8PhCN$ (8). A mixture of phen (0.50 mmol; 0.10 g) and bipm (0.25 mmol; 0.040 g) dissolved in Me_2CO (20 mL) was added to a solution of complex **A** (0.50 mmol; 0.23 g) in 30 mL Me_2CO. The reaction mixture was refluxed for 4 h. Upon standing undisturbed for three days, an orange-brown solid precipitated and was collected by filtration. The product was washed with Me_2CO and then with Et_2O and dried under vacuum.

2.3.8. $[Pt_4(\mu\text{-bipm})_3(ox)_2]Cl_4 \cdot H_2O \cdot 2PhCN$ (9). Potassium oxalate (hydrated, 1.0 mmol; 0.19 g) in H_2O (15 mL) was added to a solution of complex **A** (1.0 mmol; 0.47 g) in MeCN (25 mL). After 10 min a solution of bipm (0.50 mmol; 0.080 g) in MeCN (5.0 mL) was added. The mixture was refluxed for 2 h, whereupon dark brown solid formed. The solid was washed with Me_2CO and then with Et_2O and dried under vacuum.

3. Results and discussion

Analytical results and product yields are summarized in table 1.

Table 1. Some physical data for the complexes.

Number	Complex	%Yield	m.p. or Dec (°C)	Color	Analysis; C	Calculated H	(Found)(%) N
1	$[Pt(\mu\text{-bipm})_2][PtCl_4] \cdot PhCN$	64	360[a]	Orange-red	29.70 (29.70)	1.66 (1.80)	12.81 (13.25)
2	$[Pt_3(\mu\text{-bipm})_2(bipm)_2]Cl_6$	75	360[a]	Red-brown	26.87 (26.49)	1.67 (1.57)	15.66 (13.97)
3	$[Pt_2(\mu\text{-bipm})(bpy)Cl_2]Cl_2$	22	290	Red	25.58 (25.55)	1.67 (1.67)	12.96 (11.93)
4	$[Pt_3(\mu\text{-bipm})_2(biq)_2]Cl_6 \cdot Me_2CO \cdot MeCN$	53	360[a]	Orange-red	39.66 (39.68)	2.63 (2.66)	10.55 (10.60)
5	$[Pt_3(\mu\text{-bipm})_2(dmg)_2]Cl_2 \cdot MeCN$	68	320	Dark-green	25.55 (26.16)	2.19 (1.93)	14.66 (14.22)
6	$[Pt_5(\mu\text{-bipm})_2(dmg)_2]Cl_8 \cdot 2PhCN$	19	360[a]	Dark-purple	29.19 (28.32)	2.19 (2.32)	13.15 (13.05)
7	$[Pt_3(\mu\text{-bipm})_2(bpy)_2]Cl_6. \cdot 2Me_2CO \cdot 6PhCN$	50	360[a]	Orange	47.50 (46.68)	3.30 (3.26)	11.60 (11.66)
8	$[Pt_4(\mu\text{-bpm})_3(phen)_2]Cl_8 \cdot 8PhCN$	34	340	Orange-brown	45.77 (45.86)	2.76 (2.74)	12.61 (12.34)
9	$[Pt_4(\mu\text{-bipm})_3(ox)_2]Cl_4 \cdot H_2O \cdot 2PhCN$	72	330	Dark-brown	28.83 (28.45)	1.72 (1.82)	9.67 (9.84)

[a] No melting point or decomposition observed at 360°C.

Table 2. Important IR frequencies for the complexes (KBr and CsI pellets; cm^{-1}).

Complex	Ring stretching (C–C, C–N)	Ring breathing	ν(Pt–Cl)	Lattice solvent frequency
1	1631w, 1585m, 1540w,1405vs	1021m	290	ν(C≡N): 2361m (free PhCN)
2	1583s, 1554w, 1405vs	1025bw	–	–
3[a]	1582s, 1548m, 1454w, 1405vs	1024m	287	–
4[b]	1581vs, 1549m, 1454w, 1405vs	1030w	–	ν(C≡N): 2300m (free MeCN); ν(C=O): 1700m (free Me_2CO)
5[c]	1583s, 1554m, 1458w, 1404vs	1028m	–	ν(C≡N): 2320m (free MeCN)
6[d]	1580s, 1550m, 1453w, 1407vs	1035m	–	ν(C≡N): 2350m (free PhCN)
7[e]	1583s, 1532w, 1483w, 1405vs	1030msh	–	ν(C≡N): 2361m (free PhCN); ν(C=O): 1701m (free Me_2CO)
8[f]	1581s, 1550w, 1403v	1030w	–	ν(C≡N): 2330m (free PhCN)
9[g]	1583bs, 1552w, 1405s	1017w	–	ν(C≡N): 2361m (free PhCN); ν(O–H) and γ(HOH): 3440bm and 1610 (free H_2O)

[a] Coordinated bpy: 1633m, 1600m, 1540w, 1510w.
[b] Coordinated biq: 1631bm, 1590m, 1513w, 1463w, 1244m, 960m, 855m.
[c] Coordinated dmg: 2930w, 1520m, 1258m 1089m.
[d] Coordinated dmg: 3465m, 2938w, 1525m, 1254m, 1093m.
[e] Coordinated bpy: 1640w, 1613w, 1560w, 1520w.
[f] Coordinated phen: 1631bm, 1608m, 1508w, 1460w, 1240m, 957m, 844m, 709w.
[g] Coordinated ox: 1706m, 1675m, 1373m, 1255w, 896w.
ν = stretching frequency; γ = H-in-plane bend; vs = very strong; s = strong; m = medium; w = weak; sh = shoulder; b = broad.

3.1. *Electrical conductivity*

The conductivity values of compounds **1** and **9** correspond to electrolytes, with a molar conductivity corresponding to a 1 : 1 dissociation for **1** and 1 : 4 for (**9**), according to literature data [27]. However, the values are less than expected attributable to the large size of the cations [28, 29]. The conductivities of **2**–**8** were not measured because of their insolubility in common solvents. A chemical test was used to check the electrolytic behavior of these compounds by using $AgNO_3$ solution, which forms turbid solution upon its addition indicating the formation of AgCl.

3.2. *IR spectra*

The characteristic IR bands for the free ligand and complexes are shown in table 2. The main features are given below:

(i) Free bipm [30, 31] exhibits two strong bands at 1567 and 1157 cm^{-1}, assigned to ring vibration modes, and another narrow and strong band at 1407 cm^{-1}. An asymmetrical doublet at *ca.* 1570 cm^{-1} is characteristic of bridged bipyrimidine [32–35]. In the spectra of the compounds studied in this paper, two bands of different intensities are observed: at *ca.* 1588 (strong) and 1532 cm^{-1} (weak) (table 2). For the prepared complexes the asymmetric doublet in the 1588–1532 cm^{-1} range (table 2) is assigned to ring vibrations of the bridging bipm [32–34]. The band at 1407 cm^{-1} shifts to higher frequencies.

(ii) The IR spectra of the complexes **5** and **6** (table 2) exhibit new medium bands at *ca.* 1520, 1258, 1089 cm^{-1} assigned to the ν(NO) and ν(CH) stretching frequencies. These bands are characteristic of bonded dmg [28, 36].

Table 3. Electronic absorption spectra (in 1×10^{-5} M DMF) of bipm and some of its complexes.[a]

Compound	λ_{max} (nm)	Band assignment	$\varepsilon \times 10^{-3}$
bipm[b]	266	LC	70.2
	288	LC	34.3
1	292	LC/MLCT	122.1
	376	MLCT	42.0
	440	MLCT/d–d	8.3
	466	MLCT/d–d	7.4
2	300br, sh	MLCT	167.7
	384br	MLCT	57.5
	415br	MLCT	61.0
	440sh	MLCT/d–d	0.2
	452sh	MLCT/d–d	0.2
4	300br	LC/MLCT	196.1
	384	MLCT	67.0
	404	MLCT	70.4
	467	MLCT/d–d	7.3
	500	MLCT/d–d	6.5
5	294br, sh	LC/MLCT	160.2
	380	MLCT	75.2
	410	MLCT	76.6
	484	MLCT/d–d	5.2
	508	MLCT/d–d	3.1
9	296br, sh	LC/MLCT	90.9
	396br	MLCT	30.4
	414br	MLCT	36.2
	452	MLCT/d–d	0.7
	460	MLCT/d–d	0.6

[a] All complexes show LC bands in the range 236–280 nm.
[b] Reference [28].

(iii) The appearance of a strong band at 1373 cm^{-1} and a medium band at 675 cm^{-1} along with the medium bands 1706 and 1675 cm^{-1} and weak bands at 1255 and 896 cm^{-1} in the IR spectrum of **9** could be due to the oxalato group [28].

(iv) The absorption at *ca.* 290 cm^{-1} (table 2) in the far IR region for complexes **1** and **3** is assigned to the ν(M–Cl) stretching frequency. The disappearance of this absorption in other complexes confirms the absence of Pt–Cl bond [37].

(v) The lattice solvent in the complexes was confirmed by the appearance of their characteristic absorption bands: (a) the absorption bands in the range 2361–2300 cm^{-1}, are characteristic of free rather than bonded PhCN and MeCN in complexes **1** and **4**–**9** [37]; (b) the appearance of a medium absorption at 1700 cm^{-1} supports the presence of lattice Me_2CO in **4** and **7** [37]; (c) The appearance of a strong to medium, broad absorption at 3440 cm^{-1} (antisymmetric and symmetric OH stretching) with a band at about 1610 cm^{-1} (HOH bending) in **9** supports the presence of lattice water [28, 37].

3.3. *Electronic absorption spectra*

The electronic absorption spectral data are summarized in table 3. Insufficient solubility of other complexes has hindered their study. The bands were assigned on the basis of earlier studies [28, 29, 33, 34]. The free bipm (table 3) exhibits two

Table 4. ^{1}H-NMR chemical shifts for 2,2′-bipyrimidine (bipm) and its complexes.[a]

Complex	NMR band shift: δ, ppm without (Hz)
bipm[b]	9.07 [d, 4H; H(6, 6′), H(4, 4′)], 7.70 [t, 2H; H(5, 5′)]
2	10.04 [d, 4H; 2H(6, 6′), μ-bipm], 9.90 [dd, 4H; 2H(4, 4′), μ-bipm], 9.65 [dd, 4H; 2H(6, 6′), ter-bipm], 9.54 [dd, 4H; 2H(4, 4′), ter-bipm], 8.58 [t, 4H; 2H(5, 5′), μ-bipm], 8.32 [t, 4H; 2H(5, 5′), ter-bipm]
5	10.14 [dd, 4H; 2H(4, 4′)], 9.84 [dd, 4H; 2H(6, 6′)], 8.45 [t, 4H; 2H(5, 5′)], 2.35 [q, 12H, CH_3 of dmg]
9[c]	10.18 [m, 4H; 2H(6, 6′)], 9.71 [m, 4H; 2H(4, 4′)], 9.42 [dd, 4H; 2H(6, 6′) and H(4, 4′)], 8.32 [m, 6H; 3H(5, 5′)]

[a] ^{1}H-NMR were obtained in DMF deuterated, at 300 MHz.
[b] ^{1}H-NMR was obtained in $CDCl_3$ [28].
[c] ^{1}H-NMR obtained in DMSO.
d, doublet; dd; doublet of doublet; t, triplet; q, quartet; m, multiplet; μ, protons of bridging bipm; ter, protons of terminal bipm.

bands, at 225 and 330 nm, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, in agreement with the literature [38, 39]. The isolated complexes show strong bands which are assigned to ligand-centered (LC) and metal–ligand charge transfer (MLCT). The weak ligand-field (d–d) transitions could not be observed or appeared as a shoulder since they may be masked by the strong MLCT bands. The latter types of transitions (MLCT and d–d) give the platinum(II) complexes their characteristic colors [40, 41].

For **1** and **2**, the bands at *ca.* 248–300 nm are assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of bipm. In addition to LC bands, broad bands in the range 292–466 nm may be assigned to metal–ligand charge transfer transitions because of the π acceptor character of bipm [42, 43]. The d–d transitions for platinum(II), at *ca.* 440 and 466 nm, are consistent with reported values for square-planar Pt(II) complexes [40, 41].

The spectrum of **4** shows many bands in the range 240–300 nm that might be attributed to LC transitions of the ligands bipm and biq. The MLCT bands are in the range 300–500 nm. The broadness of the MLCT peaks at 467 and 500 may indicate the presence of d–d bands underlying MLCT bands.

Complex **5** exhibits bands at 248, 278 and 294 nm that are attributed to LC transitions. The MLCT transitions are observed in the range 294–508 along with the shoulders at 484 and 508 that are assigned to d–d transitions of Pt(II) in a square-planar arrangement.

For multinuclear complex **9**, LC bands are observed in the range 236–296 nm along with broad bands in the range 296–460 nm. The d–d transitions are observed in this complex at 452 and 460 nm revealing the square planar environment [40, 41].

3.4. ^{1}H and ^{13}C NMR spectra

The ^{1}H and ^{13}C NMR spectral data for some of the complexes are given in tables 4 and 5, respectively. The solubility problems of other complexes prevented the measurement of their spectra.

The numbering scheme of the ligand protons in the chelate and bis-chelate complexes is given in figure 2. Upon coordination, the (H_6, $H_{6'}$) and (H_4, $H_{4'}$) protons become chemically non-equivalent. It can be seen from the spectral data (table 4) that the peaks due to these protons appear as two overlapping doublets (doublet of doublet) or multiplets (table 4), rather than as a doublet as in the free ligand [39].

Table 5. ^{13}C-NMR chemical shifts for 2,2′-bipyrimidine (bipm) and its complexes.

Complex	NMR band shift: δ, ppm (Hz)
bipm[a]	162.21 (C_2, $C_{2'}$), 157.96 (C_4, $C_{4'}$, C_6, $C_{6'}$), 121.47 (C_5, $C_{5'}$)
2[b]	163.73 ($2C_2$, $2C_{2'}$, μ-bipm), 162.32 ($2C_2$, $2C_2$, ter-bipm), 159.94 ($2C_6$, $2C_{6'}$, μ-bipm), 155.37 ($2C_4$, $2C_{4'}$, μ-bipm), 155.14 ($2C_6$, $2C_{6'}$, ter-bipm), 154.97 (C_4, $C_{4'}$, ter-bipm), 124.74 ($2C_5$, $2C_{5'}$, μ-bipm and $2C_5$, $2C_{5,}$ ter-bipm)
5[b]	162.87 ($2C_2$, $2C_{2'}$), 160.64 ($2C_4$, $2C_{4'}$), 155.64 ($2C_6$, $2C_6$), 125.36 ($2C_5$, $2C_{5'}$), 20.47 (C-methyl of dmg)
9[c]	162.50 (C-O of oxalate), 160.45 ($2C_2$, $2C_{2'}$), 159.74 (C_2, $C_{2'}$), 157.51 ($2C_6$, $2C_{6'}$), 157.44 ($2C_4$, $2C_{4'}$), 155.75 (C_4, $C_{4'}$, C_6, $C_{6'}$), 125.07 ($2C_5$, $2C_{5'}$), 124.97 (C_5, $C_{5'}$)

[a] ^{13}C-NMR was obtained in $CDCl_3$ [28].
[b] ^{13}C-NMR was obtained in DMF.
[c] ^{13}C-NMR was obtained in DMSO.
μ, ^{13}C of bridging bipm; ter, ^{13}C of terminal bipm.

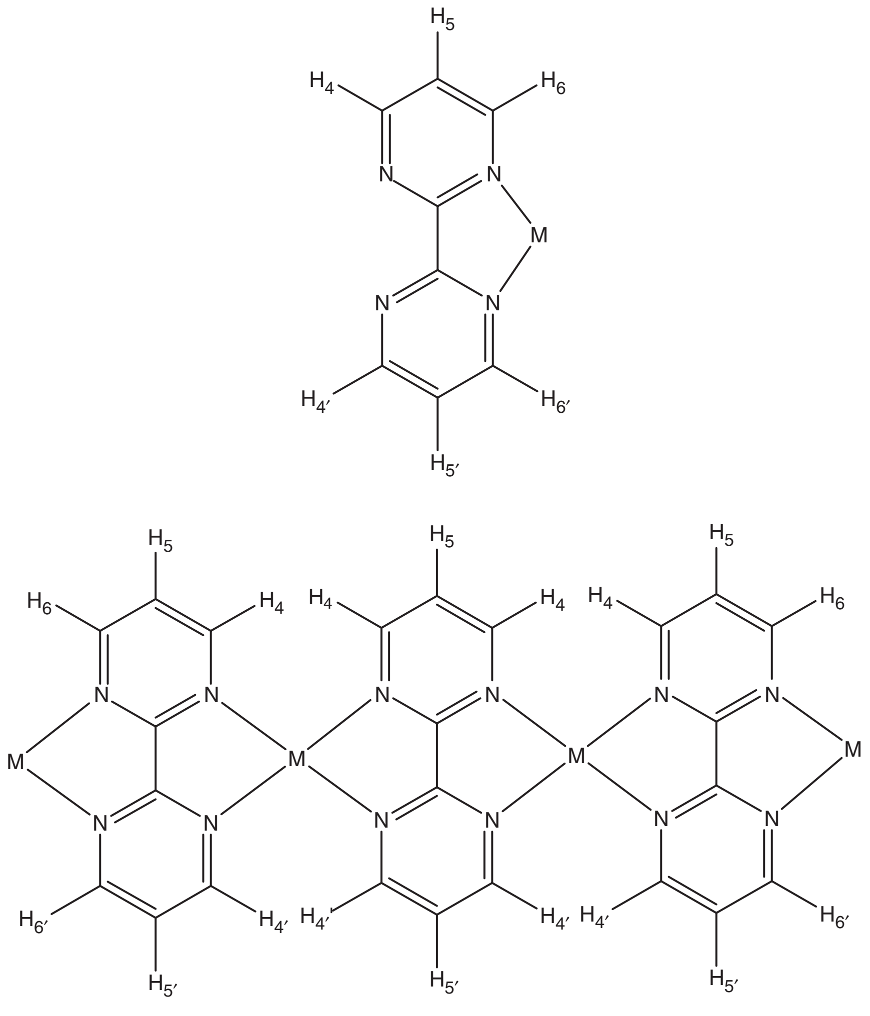

Figure 2. The numbering scheme of the ligand protons in the chelate and bis-chelate complexes.

Moreover, the protons (H_6, $H_{6'}$), which are directed toward the electronegative substituents (ox, dmg, etc.), are expected to be the most deshielded protons [28, 29, 36, 44] as shown in table 4.

The ^{13}C NMR spectra of the polymetallic complexes show additional signals corresponding to the bridging bipm and other coordinated ligands. The signals increase as the number of bridging bipm ligands increases as bipm in the center is different from terminal (table 5). The ($C_2, C_{2'}$) carbons are expected to be most deshielded since they are between the two donating nitrogen atoms. The ($C_6, C_{6'}$) are also more deshielded than ($C_4, C_{4'}$) since they are close to the electronegative susbstituents that are bonded to the metal.

The ^{13}C spectrum of complex **2** shows seven signals corresponding to seven different types of carbon; three corresponding to bridging bipm (163.73 ppm, $2C_2$, $2C_{2'}$; 159.94 ppm, $2C_6$, $2C_{6'}$; 155.37 ppm, $2C_4$, $2C_{4'}$) and three signals for terminal bipm (162.32 ppm, $2C_2$, $2C_{2'}$; 155.14 ppm, $2C_6$, $2C_{6'}$; 154.97 ppm, $2C_4$, $2C_{4'}$) and one signal at 124.74 ppm, corresponding to $4C_5$, $4C_{5'}$) terminal and bridging bipm.

^{13}C NMR for complex **9** shows eight signals corresponding to eight different types of carbon atoms, three for the central bridging bipm (159.74 ppm, C_2, $C_{2'}$; 155.75 ppm, C_4, $C_{4'}$, C_6, $C_{6'}$; 125.07 ppm, C_5, $C_{5'}$) and four for the terminal bridging bipm (160.45 ppm, $2C_2$, $2C_{2'}$; 157.51 ppm, $2C_6$, $2C_{6'}$; 157.44 ppm, $2C_4$, $2C_{4'}$; 124.97 ppm, $2C_5$, $2C_{5'}$). It also shows one additional signal due to the carbon atoms of the coordinated oxalate anion at 162.50 ppm [28, 29, 45]. The latter peak is shifted upfield as compared to the free ligand [28, 29, 45].

Complex **5** shows five signals indicating five types of carbon atom. The signals at 162.87, 160.64, 155.64 and 125.36 ppm may be attributed to ($2C_2$, $2C_{2'}$), ($2C_4$, $2C_{4'}$), ($2C_6$, $2C_{6'}$) and ($2C_5$, $2C_{5'}$), respectively; the fifth additional peak at 20.47 ppm (2-CH_3) for the coordinated dmg.

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