NMR STUDIES OF SOME Zn AND Cd COORDINATION COMPOUNDS BEARING 1,2-CICLOHEXANEDIONEDIOXIME

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Abstract. A series of homobi- and polynuclear zinc and cadmium coordination compounds supported by 1,2-cyclohexanedionedioxime (nioxime, $NioxH_2$) and bridging bidentate ligands: 4,4'-bipyridyl (bpy), 1,2-bis(4-pyridyl) ethane (bpe), 1,3-bis(4-pyridyl) propane (bpp) and dipyridyl sulphide (dps) have been characterized by the experimental techniques of ^1H and ^{13}C NMR spectroscopy. Individual NMR data of the compounds are consistent with their assignment as complexes.

Introduction

Nowadays the state of the art in analytical technologies is frequently found in the bioanalytical area, NMR spectroscopy being amongst the fast, effective and information rich methods for solving a wide range of essential purposes for human health [1-5]. Nevertheless, it still remains one of the most important analytical tools available to the classical chemist. A unique and powerful methodology of NMR for the characterization of the self-assembled complexes and the investigation of their dynamic behaviour in solution has been reviewed in a comprehensive manner [6].

Metal-organic frameworks are one of the important domains of materials science due to their useful properties that are continuously explored in gas storage, chemical separation, catalysis and luminescence. Recently the fabrications of metal-organic frameworks have been reported, whose chemical composition and shape of building units can be multiply varied within a particular structure and may lead to materials that offer a synergistic combination of properties [7]. In the light of this, designing strategies for assembling from mono- to polynuclear compounds for capitalization of their application potential is one of the priority directions in coordination chemistry.

Zinc and cadmium coordination compounds with a varied molecular composition and architecture, possessing different convenient properties, have found diverse applications, primarily related to photochemistry and luminescence [8-11].

It should be mentioned that the literature data on zinc compounds containing oxime ligands are scarce and almost missing regarding the cadmium compounds [12-14]. Mononuclear zinc and cadmium complexes are known with neutral mono- and dioximes that have been synthesized and studied in the presence of organic and inorganic anions [15,16]. A homologous series of Zn bimetallic complexes bridged by neutral, radical anionic and dianionic 4,4'-bipyridine has been reported [17]. Bimetallic zinc complexes supported by salicilaldiminato and anilido-aldimine ligands were targeted [18], which can potentially mimic phosphomonoesterase activity in protic media [19].

In search for the methods of obtaining novel materials endowed with valuable properties, new synthetic approaches were recently developed that include tuning the dimensionality from the low nuclearity complexes decorated by oxime ligands to polynuclear compounds [20-24]. Our contribution to the Zn- and Cd/oxime chemistry has demonstrated the efficacy of the oxime/anion/bipyridyne "blend" approach that resulted in the mixed-ligand discrete complexes of different nuclearity. In these articles the synthesis, some mechanistic considerations were discussed, as well as various properties, such as: supramolecular isomerism, chirality, luminescence and adsorption capacity for

homobi- and polynuclear zinc and cadmium coordination compounds supported by $NioxH_2$ and bridging bidentate ligands: bpy, bpe, bpp and dps **1-14** (Table 1), their structures being confirmed by elemental analyses, IR-spectroscopy and X-ray analyses.

Complex		Reference
Dinuclear polymers		
$[Zn_2(CH_3COO)_4(NioxH_2)_2(H_2O)_2bpy]$	**1**	[20]
$[Cd_2(CH_3COO)_4(NioxH_2)_2(H_2O)_2bpy]$	**2**	[20]
$[Cd_2(HCOO)_4(NioxH_2)_2(H_2O)_2bpy]$	**3**	[20]
$[Cd_2(CH_3COO)_4(NioxH_2)_2(H_2O)_2bpe]$	**4**	[22]
Polymers containing SO_4^{2-} anion		
$\{[Zn(NioxH_2)(SO_4)bpy]\cdot0.5H_2O\cdot DMF\}_n$	**5**	[21]
$\{[Cd(NioxH_2)(SO_4)bpy]_3(NioxH_2)(H_2O)_3\}_n$	**6**	[20]
$[Zn(NioxH_2)(SO_4)bpe]_n$	**7**	[21]
$[Cd(NioxH_2)(SO_4)bpe]_n$	**8**	[22]
Polymers without SO_4^{2-} anion		
$[Zn(CH_3COO)_2(NioxH_2)(H_2O)bpe]_n$	**9**	[22]
$\{[Cd(HCOO)_2(NioxH_2)bpe]\cdot DMF\}_n$	**10**	[24]
$[Cd(HCOO)_2(NioxH_2)bpp]_n$	**11**	[23]
$[Zn(CH_3COO)_2(NioxH_2)dps]_n$	**12**	[24]
$[Cd(CH_3COO)_2(NioxH_2)dps]_n$	**13**	[24]
$[Cd(HCOO)_2(NioxH_2)dps]_n$	**14**	[24]

The current report furnishes complementary data on the coordination compounds **1-14**. For the first time, the spectral ^{1}H and ^{13}C NMR individual characteristics for complexes **1-14** are presented. The diamagnetic nature of these coordination compounds allowed the assignment of all ^{1}H and ^{13}C signals in the respective spectra. The signals confirming ligand-metal coordination are put into discussion, in connection with the corresponding signals in free ligands.

Experimental

Complexes **1-14** were prepared according to the reported synthetic protocols (Table 1).

NMR spectroscopy

NMR spectra were recorded on a Bruker AVANCE 400 spectrometer equipped with a 5-mm broadband reverse probe with field *z* gradient, operating at 400.13 and 100.61 MHz for ^{1}H and ^{13}C nuclei, respectively. DMSO-*d6* (isotopic enrichment 99.95%) was used as solvent, containing tetramethylsilane (TMS) as an internal standard. Chemical shifts (*δ*) are reported in parts per million (ppm) and are referenced to the residual non-deuterated solvent peak (2.50 ppm for ^{1}H and 39.50 ppm for ^{13}C). The 1D and 2D NMR experiments were performed through standard pulse sequences.

DOSY NMR experiments. The spectra were recorded on a Bruker Avance 400 spectrometer,

at 9.395 tesla, at the resonating frequency of 400.13 MHz for ^{1}H nuclei, using a BBI Bruker 5 mm gradient probe. The temperature was regulated at 298 K and no spinning was applied to the NMR tube. The diffusion NMR experiments were performed with a 2D sequence for diffusion measurement using double stimulated echo for convection compensation (dstebpgp3s), using bipolar gradients. The bipolar gradient duration and the diffusion time were in the range of 1 to 1.5 ms and 200 ms, respectively. The evolution of the pulsed-field gradient during the NMR diffusion experiments was established in 32 steps, applied linearly between 1 and 50 Gcm^{-1}. Data analysis was performed using Bruker TOPSPIN software.

Results and discussion

Figure 1 depicts the used atom numbering for description of the chemical shifts of the ^{1}H and ^{13}C nuclei, as follows: in dinuclear complexes **1-4** - as shown in structure **A**, in polymers **5-10** - as shown in structure **B**, in polymer **11** - as shown in structure **C**, and in polymers **12-14** - as shown in structure **D**.

NMR characteristics for complexes **1-14** have been obtained on the basis of their 1D (^{1}H, ^{13}C, DEPT-135') and 2D homo-(^{1}H/^{1}H COSY-45') and heteronuclear (^{1}H/^{13}C HSQC and ^{1}H/^{13}C HMBC) correlation spectra. For comparison, the chemical shifts of ^{1}H and ^{13}C NMR nuclei in ligands are presented (Table 2). All the ^{1}H and ^{13}C NMR signals are given for binuclear complexes **1-4** and the data for monomers of polymeric compounds **5-14** are presented, as well (Tables 3-5). The relative areas of signals are proportional to the number of hydrogen atoms in one structural unit of the compounds.

Nioxime moiety

The ^{1}H NMR spectra of the compounds under discussion **1-14** contain the characteristic signals of the coordinated $NioxH_2$, except for the polymer **11** (Table 5). The resonances of nioxime protons showed some variation with respect to the free ligand that was more noticeable for oxime protons. Thus, in the ^{1}H spectra of complexes **1-14** the methylene groups were identified by the multiplets centred in 1.53–1.72 and 2.47–2.70 ppm regions (Tables 2-5). The resonances of these methylene carbon atoms vary insignificantly for compounds **1-14**, being found in their ^{13}C NMR spectra at 21.3–22.1 and 24.6–25.1 ppm, respectively. These values practically remain in the range of the data characterizing the free $NioxH_2$ (Table 1).
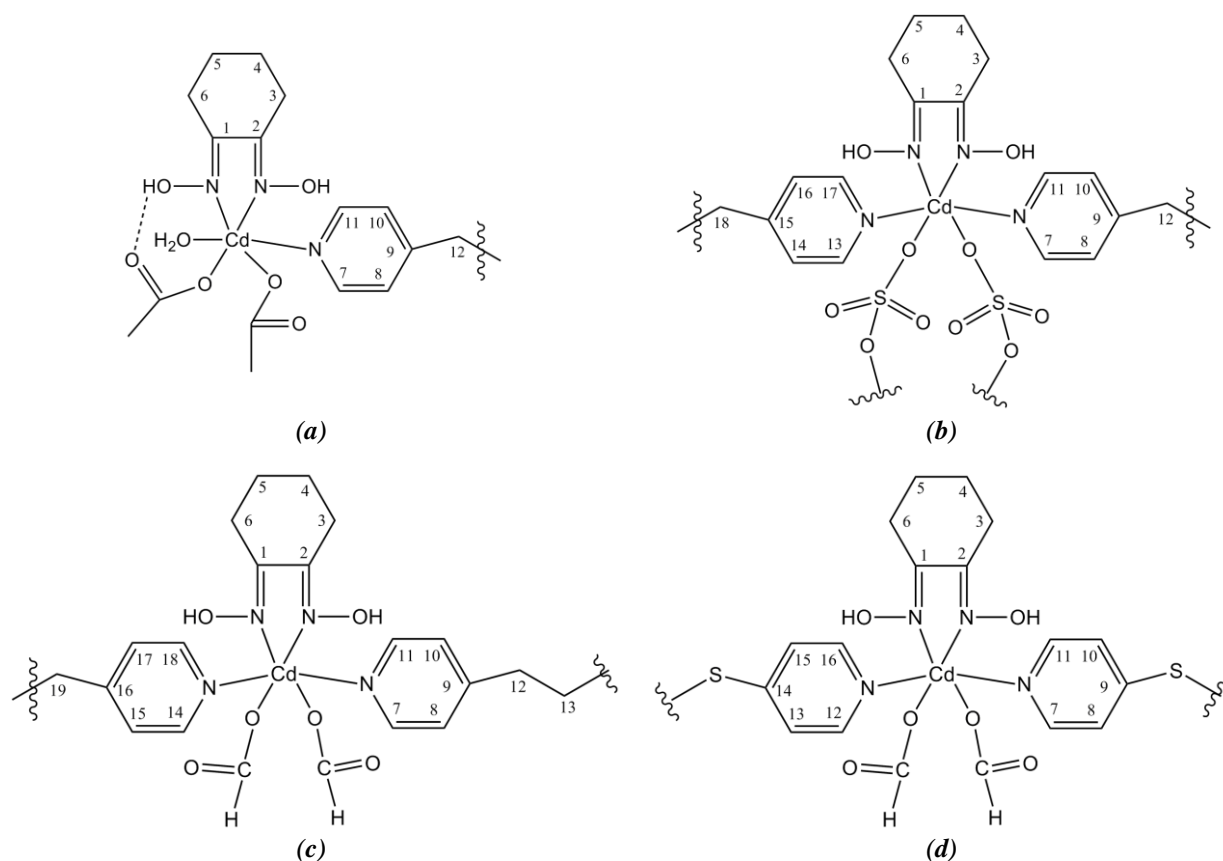
(a)

(b)

(c)

(d)

Figure 1. One unit in the structure of dimer 4 *(a)*, polymer 8 *(b)*, polymer 11 *(c)* and polymer 14 *(d)*.

Table 2

^{1}H and ^{13}C NMR spectral data for ligands (δ ppm; *J*, Hz) in DMSO-d_6 solutions.

NMR data[1] Ligand[2]	^{1}H NMR	^{13}C NMR
NioxH$_2$	1.54 (m, 4H, 2CH$_2$), 2.49 (m, 4H, 2CH$_2$), 11.17 (br. s, 2H, N-OH$_{exchangeable}$)	22.0 C(4,5), 24.9 C(3,6), 152.2 C(1,2)
bpy[3]	7.82 (app.dd, 4H, *J*= 4.5, 1.6, C(3,5 and 3',5')H), 8.72 (app.dd, 4H, *J*= 4.5, 1.6, C(2,6 and 2',6')H)	121.8 C(3,5 and 3',5'), 144.8 C(4 and 4'), 151.0 C(2,6 and 2',6')
bpe	2.93 (s, 4H, ethylene bridge), 7.25 (app.dd, 4H, *J*= 4.4, 1.6, C(3,5 and 3',5')H), 8.43 (app.dd, 4H, *J*= 4.4, 1.6, C(2,6 and 2',6')H)	34.8 (ethylene), 124.5 C(3,5 and 3',5'), 149.8 C(2,6 and 2',6'), 150.3 C(4 and 4')
bpp	1.89 (q, 2H, *J*= 7.7, CH$_2$), 2.60 (t, 4H, *J*= 7.7, CH$_2$), 7.23 (app.dd, 4H, *J*= 4.6, 1.6, C(3,5 and 3',5')H), 8.44 (app.dd, 4H, *J*= 4.6, 1.6, C(2,6 and 2',6')H)	30.6, 34.2 (propane), 124.4 C(3,5 and 3',5'), 149.9 C(2,6 and 2',6'), 151.2 C(4 and 4')
dps	7.53 (app.dd, 4H, *J*= 4.6, 1.5, C(3,5 and 3',5')H), 8.50 (app.dd, 4H, *J*= 4.6, 1.5, C(2,6 and 2',6')H)	120.6 C(3,5 and 3',5'), 146.2 C(4 and 4'), 150.4 C(2,6 and 2',6')

[1] *s: singlet; br. s: broad singlet; app. dd: apparent doublet of doublets; m: multiplet; t: triplet; q: quartet.*

[2] *for NioxH$_2$ the atom numbering was used, as depicted in Figure 1.*

[3] *for bpy, bpe, bpp and dps the pyridine atom numbering was used.*

Signals of oxime protons in complexes **1-14** were a clear proof of the ligand/metal coordination. Thus, in NioxH$_2$ oxime protons resonate at 11.17 ppm as a broad singlet, whilst in complexes **1-14** the corresponding singlets are often shifted downfield, being found in the ^{1}H NMR spectra in the range of 11.20-13.37 ppm (Tables 2-5 and Figure 2). This confirms that coordination of the ligand to the metal occurs with

the participation of oximic nitrogen atoms: coordination enhances the electron depletion of oxime proton, *i.e.* deshields its nucleus, moving the corresponding resonance to higher frequencies. At the same time, the characteristic shape of signal - broad singlet - attests the presence of intra- and intermolecular hydrogen atom bonds, as it was also documented by IR and X-ray analyses [20-24]. According to the

^{13}C NMR spectra, the peaks for the nuclei of azomethine carbon atoms in complexes **1-14** do not markedly differentiate from the corresponding chemical shifts in the free ligand, being found in the range of 150.4-152.5 ppm *versus* 152.2 ppm for NioxH$_2$ (Table 1 and Tables 2-5 for comparison).

Table 3

^{1}H and ^{13}C NMR spectral data for dinuclear polymers 1-4 (δ ppm; *J*, Hz)[1,2] in DMSO-*d*$_6$ solutions.

NMR data / Complex	^{1}H NMR	^{13}C NMR
1	1.55 (m, 8H, C(4,5 and 4',5')H$_2$), 1.84 (s, 12H, CO*CH$_3$*), 2.52 (m, 8H, C(3,6 and 3',6')H$_2$), 7.86 (app.dd, 4H, *J*= 4.5, 1.7, C(8,10 and 8',10')H), 8.73 (app.dd, 4H, *J*= 4.5, 1.7, C(7,11 and 7',11')H), 11.62 (br. s, 4H, N-OH$_{exchangeable}$)	21.9 C(4,5 and 4',5'), 22.6 (CO*CH$_3$*), 24.9 C(3,6 and 3',6'), 121.6 C(8,10 and 8',10'), 144.7 C(9 and 9'), 150.8 C(7,11 and 7',11'), 151.9 C(1,2 and 1',2'), 176.4 (*C*OCH$_3$)
2	1.59 (m, 8H, C(4,5 and 4',5')H$_2$), 1.88 (s, 12H, CO*CH$_3$*), 2.54 (m, 8H, C(3,6 and 3',6')H$_2$), 7.85 (app.dd, 4H, *J*= 4.5, 1.7, C(8,10 and 8',10')H), 8.72 (app.dd, 4H, *J*= 4.5, 1.7, C(7,11 and 7',11')H), 13.60 (br. s, 4H, N-OH$_{exchangeable}$)	21.4 C(4,5 and 4',5'), 23.5 (CO*CH$_3$*), 24.8 C(3,6 and 3',6'),121.7 C(8,10 and 8',10'), 144.8 C(9 and 9'), 150.5 C(1,2 and 1',2'), 150.8 C(7,11 and 7',11'), 177.6 (*C*OCH$_3$)
3	1.59 (m, 8H, C(4,5 and 4',5')H$_2$), 2.55 (m, 8H, C(3,6 and 3',6')H$_2$), 7.84 (app.dd, 4H, *J*= 4.4, 1.6, C(8,10 and 8',10')H), 8.30 (s, 4H, OCO*H*), 8.72 (app.dd, 4H, *J*= 4.4, 1.6, C(7,11 and 7',11')H), 13.11 (br. s, 4H, N-OH$_{exchangeable}$)	21.3 C(4,5 and 4',5'), 24.6 C(3,6 and 3',6'),121.5 C(8,10 and 8',10'), 144.6 C(9 and 9'), 150.7 C(7,11 and 7',11'), 150.8 C(1,2 and 1',2'), 167.9 (O*C*OH)
4	1.59 (m, 8H, C(4,5 and 4',5')H$_2$), 1.85 (s, 12H, CO*CH$_3$*), 2.53 (m, 8H, C(3,6 and 3',6')H$_2$), 2.95 (s, 4H, C(12 and 12')H$_2$), 7.27 (app.dd, 4H, *J*= 4.4, 1.6, C(8,10 and 8',10')H), 8.44 (app.dd, 4H, *J*= 4.4, 1.6, C(7,11 and 7',11')H), 12.92 (br. s, 4H, N-OH$_{exchangeable}$)	21.6 C(4,5 and 4',5'), 22.8 (CO*CH$_3$*), 24.8 C(3,6 and 3',6'), 34.8 (C(12 and 12'), 124.4 C(8,10 and 8',10'), 149.8 C(7,11 and 7',11'), 150.2 C(9 and 9'), 150.9 C(1,2 and 1',2'), 177.5 (*C*OCH$_3$)

[1] *s: singlet, br. s: broad singlet; app. dd: apparent doublet of doublets, m: multiplet.*

[2] *here the number of protons is presented for both units of binuclear complexes **1-4**. Integration of the signals in ^{1}H NMR spectra offers information regarding one structure unit, the binuclearity of complexes being proved by X-ray data, as stated before [20,22]. For numbering the atoms of the second structural unit, the prime symbol was used.*

Table 4

^{1}H and ^{13}C NMR spectral data for polymers containing SO$_4^{2-}$ anion 5-8 (δ ppm; *J*, Hz)[1] in DMSO-*d*$_6$ solutions.

NMR data / Complex	^{1}H NMR	^{13}C NMR
5	1.56 (m, 4H, C(4,5)H$_2$), 2.51 (m, 4H, C(3,6)H$_2$), 2.73 (s, 3H, DMF), 2.89 (s, 3H, DMF), 7.86 (app.dd, 4H, *J*= 4.5, 1.5, C(8,10 and 14,16)H), 7.95 (s, 1H, DMF), 8.74 (app.dd, 4H, *J*= 4.5, 1.5, C(7,11 and 13,17)H), 11.50 (br. s, 2H, N-OH$_{exchangeable}$)	21.9 C(4,5), 24.9 C(3,6), 30.7 and 35.7 (DMF), 121.5 C(8,10 and 14,16), 144.6 C(9 and 15), 150.7 C(7,11 and 13,17), 152.1 C(1,2), 162.7 (DMF)
6[2]	1.54 (m, 4H, C(4,5)H$_2$), 2.51 (m, 4H, C(3,6)H$_2$), 7.83 (app.dd, 4H, *J*= 4.4, 1.6, C(8,10 and 14,16)H), 8.73 (app.dd, 4H, *J*= 4.4, 1.6, C(7,11 and 13,17)H), 11.16 (br. s, 2H, N-OH$_{exchangeable}$)	22.1 C(4,5), 24.9 C(3,6), 121.5 C(8,10 and 14,16), 144.6 C(9 and 15), 150.7 C(7,11 and 13,17), 152.3 C(1,2)
7	1.56 (m, 4H, C(4,5)H$_2$), 2.48 (m, 4H, C(3,6)H$_2$), 2.95 (s, 4H, C(12 and 18)H$_2$), 7.26 (app.dd, 4H, *J*= 4.4, 1.4, C(8,10 and 14,16)H), 8.44 (app.dd, 4H, *J*= 4.4, 1.4, C(7,11 and 13,17)H), 11.25 (br. s, 2H, N-OH$_{exchangeable}$)	22.0 C(4,5), 24.9 C(3,6), 34.7 (C(12 and 18), 124.3 C(8,10 and 14,16), 149.6 C(7,11 and 13,17),150.2 C(9 and 15), 152.2 C(1,2)
8	1.56 (m, 4H, C(4,5)H$_2$), 2.49 (m, 4H, C(3,6)H$_2$), 2.95 (s, 4H, C(12 and 18)H$_2$), 7.26 (app.dd, 4H, *J*= 4.5, 1.5, C(8,10 and 14,16)H), 8.44 (app.dd, 4H, *J*= 4.5, 1.5, C(7,11 and 13,17)H), 11.27 (br. s, 2H, N-OH$_{exchangeable}$)	21.7 C(4,5), 24.6 C(3,6), 34.5 (C(12 and 18), 123.9 C(8,10 and 14,16), 149.2 C(7,11 and 13,17),149.5 C(9 and 15), 152.5 C(1,2)

[1] *s: singlet, br. s: broad singlet; app. dd: apparent doublet of doublets, m: multiplet.*

[2] *only protons of the coordination sphere are described.*

^{1}H and ^{13}C NMR spectral data for polymers 9-14 (δ ppm; J, Hz)[1] in DMSO-d_6 solutions.

NMR data / Complex	^{1}H NMR	^{13}C NMR
9	1.56 (m, 4H, C(4,5)H$_2$), 1.84 (s, 6H, COCH$_3$), 2.52 (m, 4H, C(3,6)H$_2$), 2.97 (s, 4H, C(12 and 18)H$_2$), 7.31 (app.dd, 4H, J= 4.4, 1.5, C(8,10 and 14,16)H), 8.45 (app.dd, 4H, J= 4.4, 1.5, C(7,11 and 13,17)H), 11.74 (br. s, 2H, N-OH$_{exchangeable}$)	21.8 C(4,5), 22.6 (COCH$_3$), 24.8 C(3,6), 34.7 (C(12 and 18), 124.4 C(8,10 and 14,16), 149.6 C(7,11 and 13,17),150.6 C(9 and 15), 151.8 C(1,2), 176.7 (COCH$_3$)
10	1.60 (m, 4H, C(4,5)H$_2$), 2.55 (m, 4H, C(3,6)H$_2$), 2.73 (s, 3H, DMF), 2.89 (s, 3H, DMF), 2.95 (s, 4H, C(12 and 18)H$_2$), 7.29 (app.dd, 4H, J= 4.5, 1.6, C(8,10 and 14,16)H), 8.32 (s, 2H, OCOH), 7.95 (s, 1H, DMF), 8.43 (app.dd, 4H, J= 4.5, 1.6, C(7,11 and 13,17)H), 13.20 (br. s, 2H, N-OH$_{exchangeable}$)	21.4 C(4,5), 24.9 C(3,6), 30.7 (DMF), 34.9 (C(12 and 18), 35.7 (DMF), 124.6 C(8,10 and 14,16), 149.8 C(7,11 and 13,17),150.7 C(9 and 15), 150.9 C(1,2), 162.7 (DMF), 168.2 (OCOH)
11[2]	1.72 (m, 4H, C(4,5)H$_2$), 2.03 (m, 2H, C(13)H$_2$), 2.70 (m, 4H, C(3,6)H$_2$), 2.74 (t, 4H, J=7.5, C(12,19)H$_2$), 7.34 (app.dd, 4H, J= 4.1, 1.5, C(8,10 and 15,17)H), 8.42 (app.dd, 4H, J= 4.1, 1.5, C(7,11 and 14,18)H), 8.48 (s, 2H, OCOH)	21.0 C(4,5), 24.3 C(3,6), 30.3 (C(13), 34.1 (C(12 and 19), 124.4 C(8,10 and 15,17), 148.5 C(7,11 and 14,18), 151.9 C(1,2), 152.9 C(9 and 16), 168.8 (OCOH)
12[3]	1.56 (m, 4H, C(4,5)H$_2$), 1.84 (s, 6H, COCH$_3$), 2.51 (m, 4H, C(3,6)H$_2$), 7.41 (app.dd, 4H, J= 4.5, 1.5, C(8,10 and 13,15)H), 8.56 (app.dd, 4H, J= 4.5, 1.5, C(7,11 and 12,16)H), 11.61 (br. s, 2H, N-OH$_{exchangeable}$)	21.9 C(4,5), 22.7 (COCH$_3$), 24.9 C(3,6), 125.0 C(8,10 and 13,15), 143.5 C(9 and 14), 150.7 C(7,11 and 12,16), 151.9 C(1,2), 177.5 (COCH$_3$)
13	1.58 (m, 4H, C(4,5)H$_2$), 1.85 (s, 6H, COCH$_3$), 2.52 (m, 4H, C(3,6)H$_2$), 7.40 (app.dd, 4H, J= 4.4, 1.6, C(8,10 and 13,15)H), 8.54 (app.dd, 4H, J= 4.4, 1.6, C(7,11 and 12,16)H), 13.37 (br. s, 2H, N-OH$_{exchangeable}$)	21.2 C(4,5), 23.2 (COCH$_3$), 24.5 C(3,6), 124.8 C(8,10 and 13,15), 143.3 C(9 and 14), 150.4 C(1,2), 150.5 C(7,11 and 12,16), 177.3 (COCH$_3$)
14	1.60 (m, 4H, C(4,5)H$_2$), 2.55 (m, 4H, C(3,6)H$_2$), 7.40 (app.dd, 4H, J= 4.5, 1.7, C(8,10 and 13,15)H), 8.30 (s, 2H, OCOH), 8.56 (app.dd, 4H, J= 4.5, 1.7, C(7,11 and 12,16)H), 13.02 (br. s, 2H, N-OH$_{exchangeable}$)	21.4 C(4,5), 24.8 C(3,6), 125.0 C(8,10 and 13,15), 143.4 C(9 and 14), 150.7 C(7,11 and 12,16), 151.1 C(1,2), 168.0 (OCOH)

[1] *s: singlet, br. s: broad singlet; app. dd: apparent doublet of doublets, m: multiplet.*
[2] *for polymer **11** NOH proton has not been detected.*
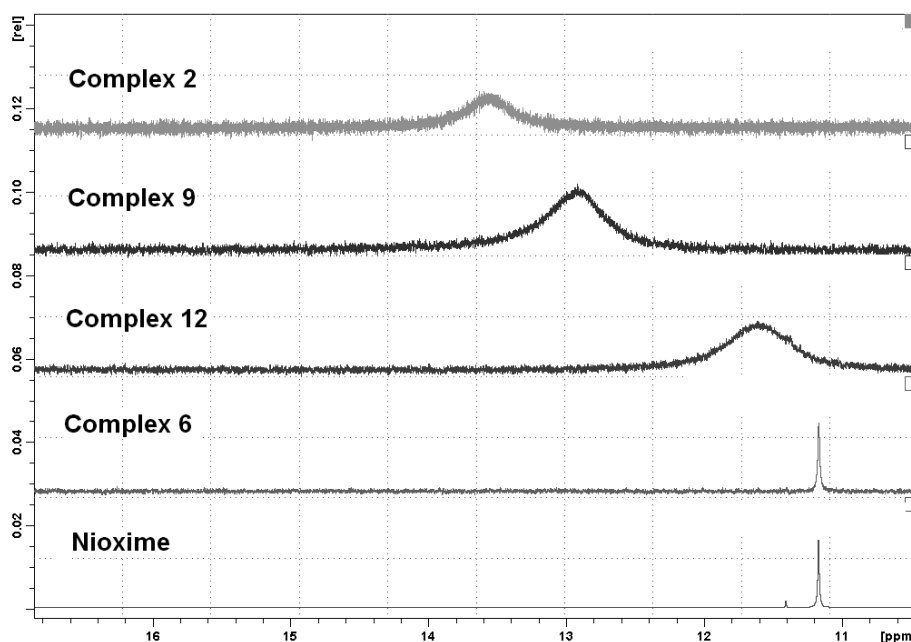[3] *C(1,2) signals found by ^{1}H/^{13}C HMBC correlation.*

Figure 2. Selected signals for oxime protons in the ^{1}H NMR spectra of NioxH$_2$ and complexes 2, 6, 9 and 12.

Pyridyl fragment

In the ^{1}H NMR spectra of compounds **1-14** the AA'XX' pattern identifying the pyridyl ring is present. Thus, the bpy moiety in the molecules of compounds **1-3, 5** and **6** is attested by the AA'XX' system in the corresponding ^{1}H spectra that appeared as two apparent doublets of doublets in aromatic region with $J=$ 4.5 and 1.7 Hz, due to the presence of *ortho-* ($\delta_H \sim$ 8.70 ppm (two AA'- parts of AA'XX' system, 4H)) and *meta-*bpy protons ($\delta_H \sim$ 7.80 ppm (two XX'- parts of AA'XX' system, 4H)). Comparison of the AA'XX' patterns in the ^{1}H spectra of complexes **1-3, 5** and **6** with the one of bpy, revealed their similarity, both as the value of chemical shift and shape of the signal (Figure 3, Tables 2-4).

Likewise, analysis of AA'XX' systems in the aromatic region of the ^{1}H NMR spectra of complexes **4, 7-9** and **10,** containing bpe as bridging ligand, showed almost a complete similarity to the corresponding region in the ^{1}H NMR spectrum of free bpe, both by the shape of the signal and its position in the ^{1}H spectrum (Tables 2-5, Figure 3). In complexes **4, 7-9** and **10,** the singlets characteristic for ethylene protons remain almost unshifted with respect to free bpe, as well (Tables 2-5).

Some comments can be made here, regarding the NMR particularities of the involved in this study bpe ligand, which is closely related to bpy. One can suppose that insertion of the ethylene moiety between pyridyl rings diminishes the diamagnetic ring current; that is why the chemical shifts of the aromatic protons in bpe are slightly upfield in comparison with bpy. *Meta-*pyridyl protons are more affected by the proximity of the ethylene fragment, their chemical shift being moved by 0.57 ppm to the region of low resonances, when compared to bpy ligand (for *ortho-* protons the upfield shift constitutes 0.29 ppm) (Table 2 and Figure 3).

^{13}C NMR spectra of compounds **1-10** showed the distinct resonances consistent with the proposed structures. According to the ^{13}C NMR spectra of complexes **1-10,** metal/bpy complexation has no distinguishable impact upon the resonance frequency of the pyridyl carbon atoms (Tables 2-4, Figures 4 and 6).

In the case of polymer **11** bpp serves as bridging ligand; the AA'XX' pattern in its ^{1}H spectrum is again rather close to that of free ligand (Tables 2, 5 and Figure 5). As observed for the bpe-containing polymeric complexes **4, 7-9** and **10**, complexation to the metal has no major impact upon the resonance frequency of the protons from neighbouring pyridyl rings. It should be mentioned, that protons of pyridyl rings in free bpp resonate at lower frequencies too, in comparison with bpy ligand (δ_H 8.44 and 7.23 ppm in bpp *versus* δ_H 8.72 and 7.82 ppm in bpy), thus demonstrating that the propane moiety also decreases the diamagnetic ring current, as it was afore-discussed for the homologous bpe ligand (Table 2). Signals of propane protons are slightly downfield in the ^{1}H spectrum of polymer **11** (δ_H 2.03 and 2.74 ppm), with respect to the signals identifying the free bpp (δ_H 1.89 and 2.60 ppm) (Tables 2 and 5).
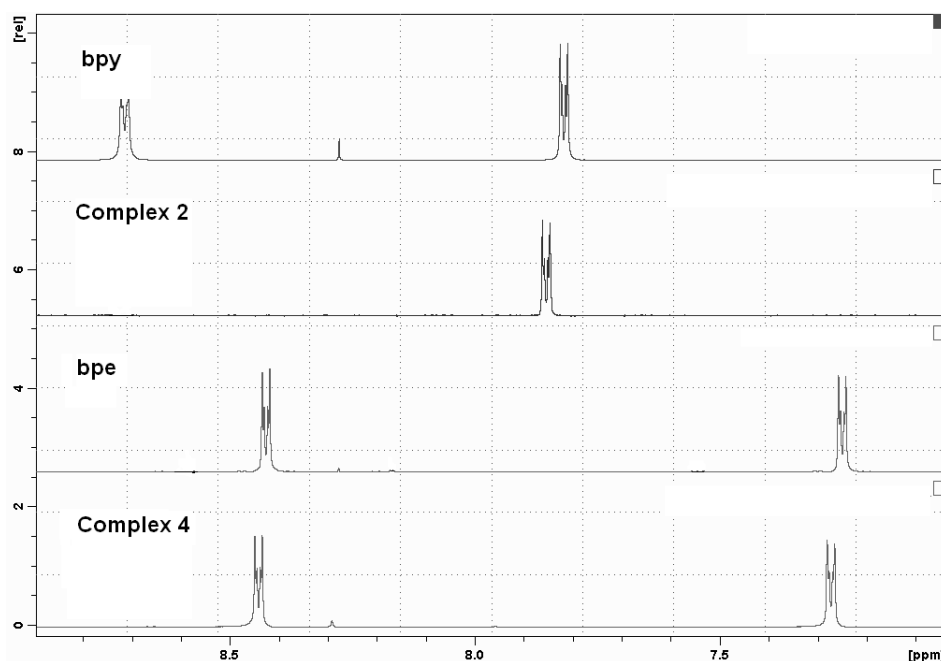

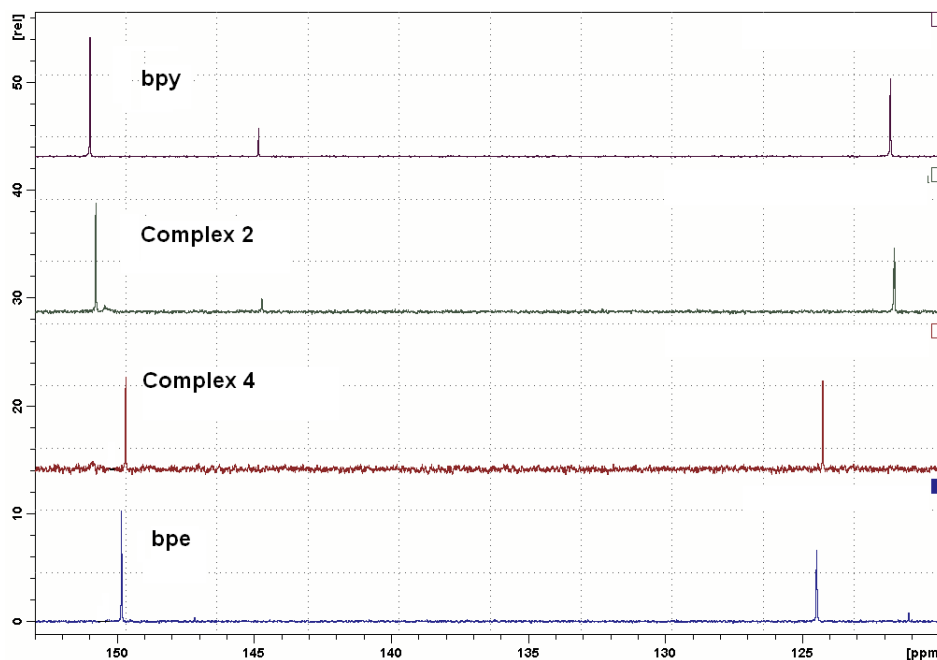**Figure 3. Aromatic region in the ^{1}H NMR spectra of complexes 2 and 4 *versus* ligands: bpy and bpe.**

Figure 4. Aromatic region in the ^{13}C NMR spectra of complexes 2 and 4 *versus* ligands: bpy and bpe.
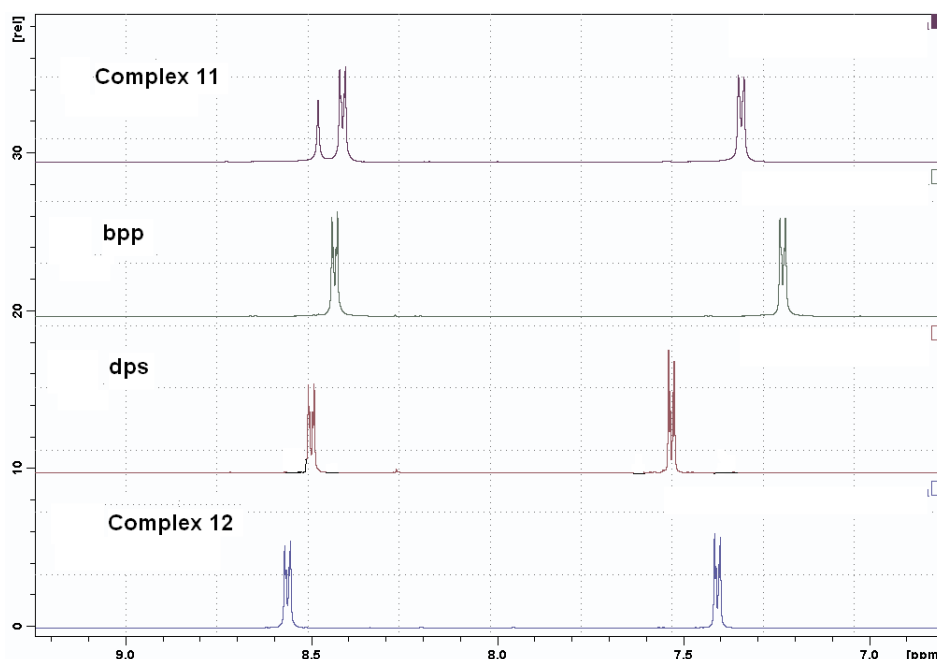

Figure 5. Aromatic region in the ^{1}H NMR spectra of complexes 12 and 11 *versus* ligands: dps and bpp.

In the ^{1}H spectrum of polymer **11** the shape of signal for magnetically equivalent protons at C(12) and C(19) remains unmodified (t, *J*= 7.5 Hz), in comparison with the corresponding signal in free bpp (t, *J*= 7.7 Hz), while the characteristic quartet for two propane protons at δ_H 1.89 ppm with the coupling constant of 7.7. Hz in bpp becomes a multiplet centred at δ_H 2.03 ppm in complex **11**. Signals of *ortho*-carbon atoms in pyridyl fragment of complex **11** are shifted upfield by 1.4 ppm, while the carbon atoms adjacent to the propane moiety resonate at a higher frequency (the downfield shift of 1.7 ppm), with respect to the corresponding signals in ^{13}C spectrum of bpp (Tables 2 and 5 and Figure 6).

Finally, we present the peculiarities observed by us of dps and dps-containing polymers **12-14**. In the AA'XX' systems from the ^{1}H NMR spectra of complexes **12-14**, a small upfield shift has been noted for the close to sulphur heteroatom *meta*-protons of pyridyl rings (by ~ 0.13 ppm), in comparison with the ^{1}H NMR data of free dps (Tables 2 and 5, Figure 5).
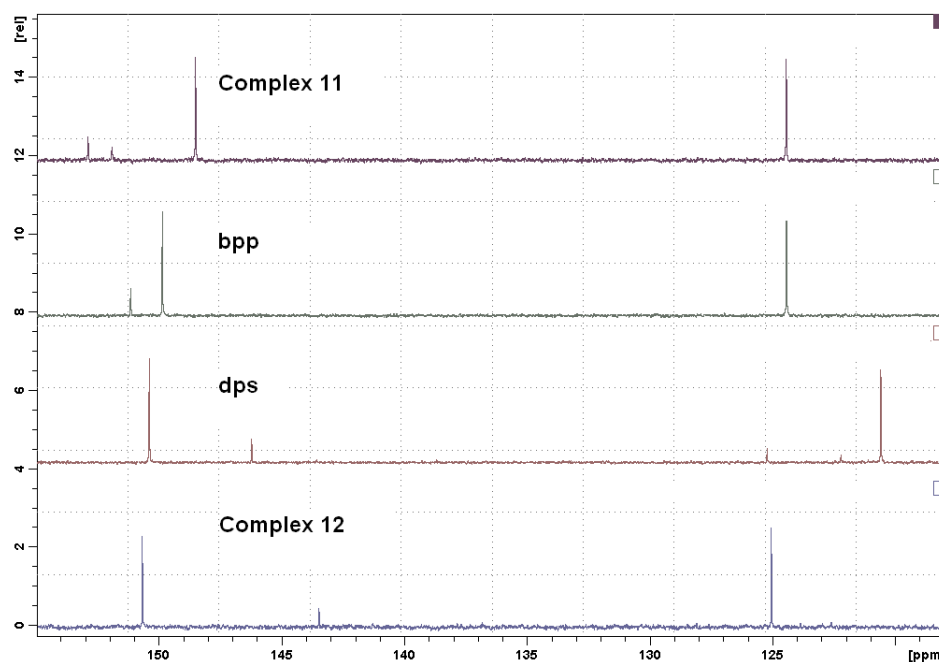
Figure 6. Aromatic region in the ^{13}C NMR spectra of complexes 12 and 11 *versus* ligands: dps and bpp.

Interestingly and differently from the bpy-, bpe- and bpp- containing complexes, the resonances of these *meta-* carbons in pyridyl moieties of polymers **12-14** were found downfield by ~4.4 ppm in the ^{13}C NMR spectra, in comparison with free dps (*e.g.*, δ_C 125.0 ppm for complex **12** *versus* δ_C 120.6 ppm for dps). Vicinal to sulphur atom pyridyl quaternary carbons, on the contrary, have shown an upfield shift (*e.g.*, δ_C 143.5 ppm for complex **12** *versus* 146.2 ppm for free dps), whilst the resonance frequency for *ortho-* pyridyl carbons does not significantly change (150.7 ppm *versus* 150.4 ppm (Tables 2 and 5, Figure 6). In our opinion, the noted specific features in the ^{13}C NMR data of complexes **12-14** can be explained by the concerted expression of the effects from the conjugation of p lone electron pairs of sulphur with neighbouring π-electron systems, and chelation. According to the classics in electrophilic aromatic substitution, in dps the electronegative sulphur atom with its two lone pairs of electrons represent a resonance donating agent that augment the electron density in the ring through resonance at C(3,5 and 3',5'; δ_C 120.6 ppm). However, in the molecules of complexes **12-14**, most probably due to the metal-dps coordination, the electron density in the aromatic rings is redistributed, the nuclei of carbons under discussion becoming deshielded (in complexes **12-14** these are nuclei of atoms C(8,10 and 13,15)), that causes the downfield shift of these nuclei (δ_C 125.0 ppm), as afore-described. Likewise, the induced by chelation electron density fluctuation can determine the

shielding of C(9 and 14) nuclei in polymers **12-14**, when compared to the respective C(4 and 4') atoms in dps.

Additional room-temperature (298 K) diffusion experiments on compound $[Zn(CH_3COO)_2(NioxH_2)dps]_n$ **12**, as well as $NioxH_2$ and dps, were also conducted to establish the structure of **12** in solution (Figure 7). The translational diffusion coefficient value (D), which is a function of the molecular size and shape [25], was determined for complex **12** showing a magnitude of 2.238×10^{-10} m^2/s. To calculate D, the Stokes-Einstein equation has been used [25]. The observed D value is significantly different to those obtained for the solutions of dps and $NioxH_2$ of the same molarities (3.09×10^{-10} m^2/s and 1.778×10^{-10} m^2/s, respectively). Thus, no dissociation of complex **12** was found in DMSO-d_6 solution. For solvent species present in solution, the following D values were calculated: 6.025×10^{-10} m^2/s (DMSO) and 7.762×10^{-10} m^2/s (H_2O).

The presence of acetate/formate ligands in the molecules of complexes **1-4** and **9-14** was duly attested by the corresponding signals in the ^1H and ^{13}C NMR spectra of compounds (Tables 3 and 5). Inclusion of the DMF molecules in the polymer matrixes of compounds **5** and **10** was ascertained by the characteristic chemical shifts for ^1H and ^{13}C nuclei of DMF that were present in the spectra of these compounds. The presence of crystallisation water in the studied complexes could not be ascertained by ^1H NMR due to signal overlapping with the dissolved in DMSO-d_6 water.
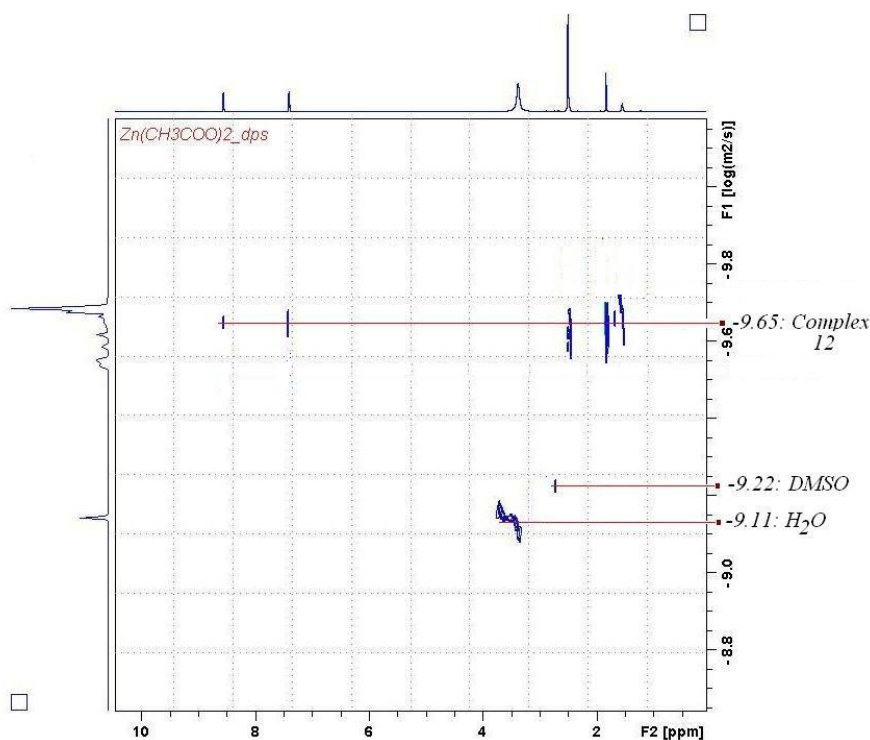
Figure 7. DOSY spectrum of complex 12.

Conclusions

Homodinuclear Zn and Cd complexes **1-4**, as well as coordination polymers **5-14** supported by 1,2-cyclohexanedionedioxime and bridging bidentate ligands: 4,4'-bipyridyl, 1,2-bis(4-pyridyl) ethane, 1,3-bis(4-pyridyl) propane and dipyridyl sulphide have been characterized by using the 1D (^{1}H, ^{13}C, DEPT-135') and 2D homo-(^{1}H/^{1}H COSY-45') and heteronuclear (^{1}H/^{13}C HSQC and ^{1}H/^{13}C HMBC) NMR experiments in DMSO-d_6 solutions. For the first time the spectral ^{1}H and ^{13}C NMR individual characteristics for complexes **1-14** are presented. The broad singlets identifying oxime protons were found to be particularly relevant for confirmation of the nioxime-metal coordination, also confirming the presence of intra- and intermolecular hydrogen atom bonds in the molecules under investigation. The resonance frequencies of the protons from the pyridyl fragments do not undergo significant changes after chelation. In the ^{13}C spectra of complexes **12-14** containing dipyridyl sulphide, noticeable change in the chemical shift for the *para-* (vicinal to sulphur) and *meta-* pyridyl carbon atoms, with respect to the free ligand, can serve as a proof of dps-metal coordination.

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