Cobalt(II) and magnesium(II) complexes with 1,3-pdta-type of ligands: influence of an alkyl substituent at 1,3-propanediamine chain on the structural and antimicrobial properties of the complex

Jelena Gitarić[a], Ivana M. Stanojević[b], Dušanka D. Radanović[c], Aurélien Crochet[d], Darko P. Ašanin[e], Vukasin Jankovic[f], Sanja Skaro-Bogojevic[f], Miloš I. Djuran[g,*] and Biljana Đ. Glišić[a,*]

[a]University of Kragujevac, Faculty of Science, Department of Chemistry, Radoja Domanovića 12, 34000 Kragujevac, Serbia; [b]University of Niš, Faculty of Agriculture in Kruševac, Kosančićeva 4, 37000 Kruševac, Serbia; [c]University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia; [d]University of Fribourg, Department of Chemistry, Chemin du Musée 9, CH-1700 Fribourg, Switzerland; [e]University of Kragujevac, Institute for Information Technologies Kragujevac, Jovana Cvijića bb, 34000 Kragujevac, Serbia; [f]University of Belgrade, Institute of Molecular Genetics and Genetic Engineering, Vojvode Stepe 444a, 11042 Belgrade, Serbia; [g]Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia

[*]Corresponding authors. *E-mail addresses*: milos.djuran@pmf.kg.ac.rs (Miloš I. Djuran); biljana.glisic@pmf.kg.ac.rs (Biljana Đ. Glišić).

ABSTRACT

To investigate how modification in the structure of 1,3-propanediamine chain of 1,3-pdta (1,3-propanediamine-*N,N,N′,N′*-tetraacetate) ligand affects the structural and biological properties of the corresponding metal complexes, two new octahedral complexes, $[Co(H_2O)_5Co(2,2\text{-diMe-}1,3\text{-pdta})]\cdot H_2O$ (**1**) and $[Mg(H_2O)_5Mg(2,2\text{-diMe-}1,3\text{-pdta})]\cdot 1.5H_2O$ (**2**) (2,2-diMe-1,3-pdta = 2,2-dimethyl-1,3-propanediamine-*N,N,N′,N′*-tetraacetate), were synthesized and characterized by IR spectroscopy and single-crystal X-ray diffraction analysis. Additionally, UV-Vis and NMR spectroscopic methods were applied for the characterization of **1** and **2**, respectively. Crystallographic data indicate that these complexes contain 2,2-diMe-1,3-pdta coordinated to the metal ion through 2 N and 4 O atoms forming $[M(H_2O)_5M'(2,2\text{-diMe-}1,3\text{-pdta})]$ complex unit (M, M′ = Co(II), Co(II) (**1**) and M, M′ = Mg(II), Mg(II) (**2**)), which is composed of $[M'(2,2\text{-diMe-}1,3\text{-pdta})]^{2-}$ and $[M(H_2O)_5O]^{2+}$ octahedra bridged by one of the axial carboxylate groups. The antimicrobial activities of **1** and **2** were evaluated against different bacteria and *Candida* spp., while their cytotoxic effect was tested on the normal human lung fibroblasts (MRC-5). The ability of **1** and **2** to inhibit formation of *C. glabrata* biofilms was also assessed. The obtained structural parameters and biological properties of the two complexes were compared to Co(II) and Mg(II) complexes with 1,3-pdta ligand.

KEYWORDS: Cobalt(II) complexes; magnesium(II) complexes; 1,3-pdta-type ligands; structural characterization; antimicrobial activity

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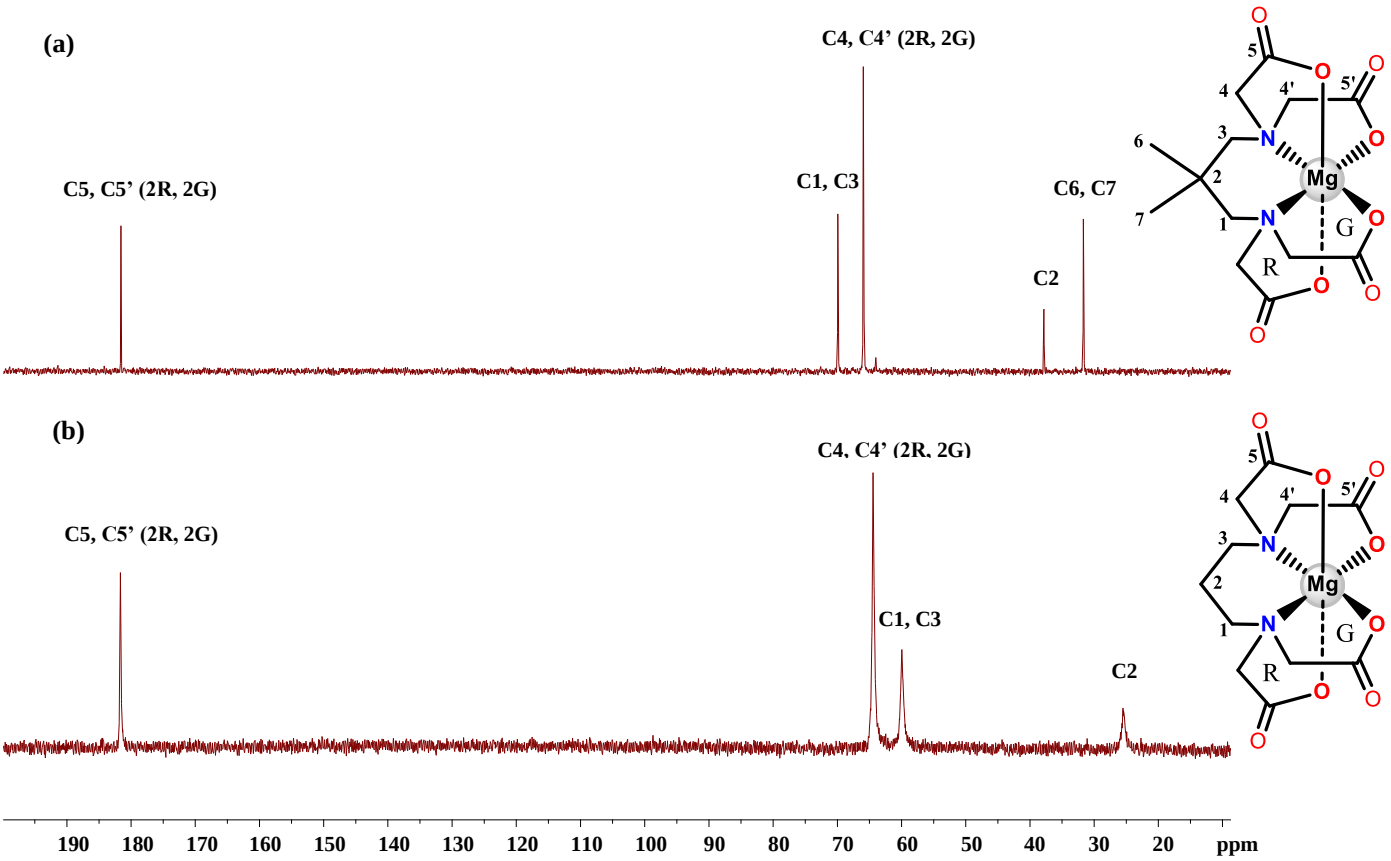

Figure S1. ^{13}C NMR spectra of $[Mg(2,2\text{-diMe-}1,3\text{-pdta})]^{2-}$ **(a)** and $[Mg(1,3\text{-pdta})]^{2-}$ **(b)** complex anions of $[Mg(H_2O)_5Mg(2,2\text{-diMe-}1,3\text{-pdta})]\cdot 1.5H_2O$ (**2**) and $[Mg(H_2O)_6][Mg(1,3\text{-pdta})]\cdot 2H_2O$ complexes.

Table S1. Details of the crystal structure determinations of complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{13}H_{30}Co_2N_2O_{14}$	$C_{13}H_{31}Mg_2N_2O_{14.5}$
Formula weight (g/mol)	556.25	496.02
Crystal system, space group	monoclinic, *C2/c*	monoclinic, *C2/c*
a (Å)	31.2713(7)	31.2752(5)
b (Å)	10.8581(2)	10.8978(2)
c (Å)	13.6012(3)	13.7754(2)
α (°)	90	90
β (°)	103.775(2)	104.3020(10)
γ (°)	90	90
V (Å^3)	4485.42(17)	4549.57(13)
F_{000}	2304	2104
Z	8	8
X-radiation, λ /Å	Cu Kα (λ = 1.54186)	Cu Kα (λ = 1.54186)
Data collect. temperat. /K	250(2)	250(2)
Calculated density (Mg/m^3)	1.647	1.448
Absorption coefficient (mm^{-1})	12.233	1.611
Crystal size (mm)	0.2 × 0.14 × 0.1	0.19 × 0.12 × 0.04
2θ range (°)	13.284 to 136.63	10.43 to 136.094
index ranges *h*, *k*, *l*	-37 ... 30, -9 ... 13, -16 ... 14	-33 … 37, -12… 12, -15 ... 10
No. of collected and independent reflections	29866, 4034	34600, 4046
R_{int}	0.0280	0.0249
Data / restraints / parameters	4034 / 3 / 304	4046 / 4 / 305
Goodness-on-fit on F^2	1.059	1.023
Final *R* indices [$I \geq 2\sigma(I)$]	R_1 = 0.0440, wR_2 = 0.1271	R_1 = 0.0308, wR_2 = 0.0856
Final *R* indices (all data)	R_1 = 0.0473, wR_2 = 0.1294	R_1 = 0.0319, wR_2 = 0.0865
Difference density: max, min (e/Å^3)	0.55, -0.55	0.31, -0.38

Table S2. Selected bond distances (Å) and valence angles (°) in complexes **1** and **2**.

	1	**2**
M	Co	Mg
M1–O1	2.069(2)	2.0288(11)
M1–O3	2.092(2)	2.0402(10)
M1–O5	2.056(2)	2.0414(11)
M1–O7	2.087(2)	2.0614(11)
M1–N1	2.137(2)	2.1970(12)
M1–N2	2.164(2)	2.2241(12)
M2–O8	2.128(2)	2.1007(11)
M2–O9	2.081(3)	2.0523(12)
M2–O10	2.050(3)	2.0324(11)
M2–O11	2.081(3)	2.0484(12)
M2–O12	2.055(3)	2.0491(12)
M2–O13	2.118(3)	2.1361(12)
O1–M1–O3	104.89(8)	109.65(4)
O1–M1–O7	91.31(10)	92.34(4)
O1–M1–N1	80.56(9)	80.28(4)
O1–M1–N2	170.81(10)	168.10(5)
O3–M1–N1	173.90(9)	169.75(5)
O3–M1–N2	79.45(9)	79.18(4)
O5–M1–O1	97.73(10)	97.50(5)
O5–M1–O3	94.83(9)	95.69(4)
O5–M1–O7	167.42(9)	164.46(5)
O5–M1–N1	81.56(9)	80.12(4)
O5–M1–N2	89.89(9)	89.31(4)
O7–M1–O3	91.25(9)	92.26(4)
O7–M1–N1	91.37(10)	89.78(4)
O7–M1–N2	80.40(9)	79.08(4)
N1–M1–N2	95.57(9)	91.36(4)
O9–M2–O8	89.98(11)	90.01(5)
O9–M2–O11	175.78(14)	177.59(6)
O9–M2–O13	89.75(16)	91.69(6)

O10–M2–O8	176.76(10)	175.78(5)
O10–M2–O9	86.82(11)	86.6
O10–M2–O11	93.96(11)	93.21(5)
O10–M2–O12	96.09(15)	97.19(6)
O10–M2–O13	89.29(13)	89.35(5)
O11–M2–O8	89.20(10)	88.26(4)
O11–M2–O13	86.12(14)	85.90(5)
O12–M2–O8	84.53(13)	85.39(5)
O12–M2–O9	91.63(15)	91.67(6)
O12–M2–O11	92.12(13)	90.74(5)
O12–M2–O13	174.45(13)	172.82(5)
O13–M2–O8	90.18(10)	88.26(4)

Table S3. Geometrical parameters describing hydrogen bond interactions in crystals of complexes **1** and **2**.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (º)
		1		
O9—H9A···O14^{i}	0.85	1.91	2.686(5)	150.7
O9—H9B···O3^{ii}	0.85	1.88	2.715(4)	165.8
O10—H10A···O5^{iii}	0.85	1.84	2.679(3)	169.0
O10—H10B···O4^{ii}	0.85	1.88	2.711(3)	165.9
O11—H11A···O2^{iv}	0.85	1.85	2.695(5)	169.2
O11—H11B···O6^{iii}	0.85	1.94	2.713(4)	150.8
O12—H12A···O1^{iv}	0.85	1.84	2.687(4)	175.2
O12—H12B···O15^{iii}	0.85	1.91	2.704(3)	154.4
O13—H13A···O7	0.86	1.91	2.657(4)	145.0
O13—H13B···O14^{v}	0.86	1.96	2.745(6)	152.4
O14—H14A···O8^{i}	0.85	2.86	3.374(6)	121.0
O14—H14B···O8	0.85	2.04	2.772(5)	143.3
O14—H14B···O12	0.85	2.69	3.414(7)	143.9
O15—H15A···O4	0.85	1.98	2.759(3)	151.5
O15—H15B···O4^{i}	0.85	1.97	2.759(3)	154.7
Symmetry codes: (i) 1−*x*, +*y*, ½−*z*; (ii) 1−*x*, 1−*y*, 1−*z*; (iii) +*x*, −1+*y*, +*z*; (iv) +*x*, 1−*y*, ½+*z*; (v) +*x*, 1−*y*, ½+*z*				
		2		
O9—H9A···O14^{i}	0.85	1.90	2.7444(17)	172.2
O9—H9B···O3^{ii}	0.85	1.92	2.7661(15)	170.6
O10—H10A···O5^{iii}	0.85	1.85	2.6870(14)	170.6
O10—H10B···O4^{ii}	0.85	1.89	2.7372(15)	173.7
O11—H11A···O6^{iii}	0.86	1.89	2.6940(16)	155.4
O11—H11B···O2^{iv}	0.86	1.89	2.7095(16)	159.6
O12—H12A···O1^{iv}	0.85	1.87	2.7174(15)	171.9
O12—H12B···O15^{iii}	0.85	1.89	2.7287(14)	169.5
O13—H13A···O7	0.86	1.87	2.6641(15)	153.3
O14—H14···O9^{i}	0.91	1.97	2.7444(17)	142.2
O14—H14A···O13^{iv}	0.85	2.02	2.8081(19)	153.3
O14—H14B···O8	0.85	2.07	2.8616(17)	154.6
O14—H14B···O12	0.85	2.74	3.325(2)	127.5
O15—H15A···O4^{i}	0.85	1.94	2.7865(15)	176.2
O15—H15B···O4	0.85	1.98	2.7865(15)	157.1
Symmetry codes: (i) 1−*x*, +*y*, ½−*z*; (ii) 1−*x*, 1−*y*, −*z*; (iii) +*x*, −1+*y*, +*z*; (iv) +*x*, 1−*y*, ½+*z*				

Table S4. IR carboxylate stretching frequencies (ν, cm^{-1}) of cobalt(II) and magnesium(II) complexes with 1,3-pdta and 2,2-diMe-1,3-pdta ligands.

Complex	ν_{asym}	ν_{sym}	Ref.
$[Co(H_2O)_6][Co(1,3\text{-pdta})]\cdot 2H_2O$	1675 (*w*), 1587 (*s*)	1477 (*m*), 1447 (*m*), 1407 (*s*), 1334 (*s*)	[4]
$[Co(H_2O)_5Co(2,2\text{-diMe-}1,3\text{-pdta})]\cdot H_2O$ (**1**)	1614 (*s*)	1483 (*w*), 1463 (*w*), 1442 (*m*), 1396 (*s*), 1340 (*m*), 1324 (*m*), 1306 (*m*)	This work
$[Mg(H_2O)_6][Mg(1,3\text{-pdta})]\cdot 2H_2O$	1687(*w*), 1597 (*s*)	1479 (*m*), 1447 (*m*), 1407 (*s*), 1335 (*s*), 1326 (*w*)	[5]
$[Mg(H_2O)_5Mg(2,2\text{-diMe-}1,3\text{-pdta})]\cdot 1.5H_2O$ (**2**)	1618 (*s*)	1444 (*m*), 1414 (*w*), 1393 (*s*), 1339 (*m*), 1325 (*m*), 1306 (*w*)	This work

asym = asymmetrical; *sym* = symmetrical; *s* = strong; *m* = medium; *w* = weak.

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Table S5. ^{13}C NMR chemical shifts for $[Mg(2,2\text{-diMe-}1,3\text{-pdta})]^{2-}$ and $[Mg(1,3\text{-pdta})]^{2-}$ complex anions of $[Mg(H_2O)_5Mg(2,2\text{-diMe-}1,3\text{-pdta})]\cdot 1.5H_2O$ (**2**) and $[Mg(H_2O)_6][Mg(1,3\text{-pdta})]\cdot 2H_2O$ complexes.

Complex anion/carbon atom (ppm)	C1, C3	C2	C4, C4'	C5, C5'	C6, C7
$[Mg(2,2\text{-diMe-}1,3\text{-pdta})]^{2-}$ (**2**)	72.73	40.65	67.79	184.39	34.49
$[Mg(1,3\text{-pdta})]^{2-}$	59.94	25.52	64.43	181.65	