## Syntheses, Spectra, Thermal Studies and Crystal Structures of Vitamin B13 Complexes of Nickel(II) with N,N,N',N'-Tetramethylethylenediamine and 2,2-Dimethylpropane-1,3-diamine

Okan Zafer Yeşilel,\*<sup>[a]</sup> Hakan Erer,<sup>[a]</sup> Necmi Dege,<sup>[b]</sup> and Orhan Büyükgüngör<sup>[b]</sup>

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Abstract. Two nickel(II) complexes of vitamin B13 (H<sub>3</sub>Or) with N,N,N',N'-tetramethylethylenediamine (tmen) and 2,2-dimethylpropane-1,3-diamine (dmpen) were synthesized and characterized by means of elemental and thermal analyses, magnetic susceptibility, and IR and UV/Vis spectroscopic studies. The crystal structures of *mer*-[Ni(HOr)(H<sub>2</sub>O)<sub>2</sub>(tmen)]·H<sub>2</sub>O (1) and [Ni(HOr)-(dmpen)<sub>2</sub>] (2) were determined by using single-crystal X-ray diffrac-

## Introduction

Vitamin B13 (Orotic acid, H<sub>3</sub>Or) is an important uracil derivative, as the effective precursor in the biosynthesis of uracil base of RNA in living organisms [1, 2]. In the last years, research in bioinorganic chemistry has revealed the important role of metal ions in most biological processes. For these reasons, some metal complexes of vitamin B13 and its derivatives have recently attracted growing attention in medicine for applications in curing syndromes related with some metal deficiencies. In addition, nickel, magnesium, palladium, and platinum orotato complexes have been screened as therapeutic agents for cancer [3, 4]. Studies showed that the presence of three different functional groups such as pyrimidine nitrogen atoms, carbonyl oxygen atoms, or carboxylate oxygen atoms makes orotate a polyfunctional ligand in coordination chemistry [5-19]. The most common coordination mode of HOr<sup>2-</sup> is ligation through a deprotonated nitrogen atom of the pyrimidine ring and a carboxylate oxygen atom so forming a fivemembered chelate ring. Crystal structures have been Ni<sup>II</sup> described for the mononuclear complexes,  $[Ni(HOr)(H_2O)(tea)] \cdot H_2O$  (tea = triethanolamine) [10],  $[Ni(HOr)(H_2O)(4-mim)_3]_2 \cdot 5H_2O$  (4-mim = 4(5)-methylimidazole) [11],  $[Ni(HOr)(H_2O)_2(im)_2]$  (imidazole) [12],

tion. In the complexes, which crystallize in the triclinic system (space group  $P\bar{1}$  for 1) and the monoclinic system (space group  $P2_1/c$  for 2), the Ni<sup>II</sup> ions exhibit a distorted octahedral coordination. Ni<sup>II</sup> ions are chelated by the deprotonated nitrogen atom of the pyrimidine ring and the oxygen atom of the carboxylate group, the distorted octahedral coordination completed by one tmen and two aqua ligands for 1 or two dmpen ligands for 2.

 $[Ni(HOr)(H_2O)_3(na)] \cdot 2H_2O$  (na = nicotine amide) [13], [Ni(HOr)(H<sub>2</sub>O)<sub>4</sub>]·H<sub>2</sub>O [14], [Ni(HOr)(bipy)(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (bipy = 2,2'-bipyridine) [15, 16],  $[Ni(HOr)(dpa)(H_2O)_2]$ .  $H_2O$  (dpa = 2,2'-bipyridylamine) [16], [Ni(HOr)(dpa)\_2].  $0.5H_2O$  [16], [Ni(HOr)(phen)(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (phen = 1,10phenanthroline) [16],  $[Ni(HOr)(dmphen)(H_2O)] (dmphen =$ 2,9-dimethyl-1-1,10-phenanthroline) [16], and [Ni(HOr)(- $(mea)_2$  (mea = monoethanolamine) [17], where orotate acts as a bidentate ligand. In the polymeric  $[Ni(HOr)(H_2O)_3]_n$ [16, 18] and  $[Ni(HOr)(NH_3)(H_2O)_2]_{\nu}$  [19] complexes, HOr<sup>2-</sup> acts as a bridging ligand. In [Ni(H<sub>2</sub>O)<sub>6</sub>](H<sub>2</sub>Or)<sub>2</sub>·2H<sub>2</sub>O [20], H<sub>2</sub>Or<sup>-</sup> does not coordinate the metal ion and behaves as a counterion. Recently, we reported the thermal decomposition of Ni<sup>II</sup>, Co<sup>II</sup>, Cu<sup>II</sup>, and Cd<sup>II</sup>-1,10-phenanthroline complexes with orotato counterions [21]. In this study, we describe the preparation and spectroscopic characterization (IR and UV/Vis) of orotato complexes of Ni<sup>II</sup> with N, N, N', N'-tetramethylethylenediamine (tmen) mer-[Ni(HOr)(H<sub>2</sub>O)<sub>2</sub>(tmen)]·H<sub>2</sub>O (1) and 2,2-dimethylpropane-1,3-diamine (dmpen), [Ni(HOr)(dmpen)<sub>2</sub>] (2). The thermal decomposition pathway of the complexes was followed by the help of thermal analysis (TG, DTG and DTA). The crystal structures of both complexes were also determined by single-crystal X-ray diffraction.

## **Results and Discussion**

#### Magnetic Susceptibility and UVIVis Spectra of 1 and 2

The electronic spectroscopic data, the assignment of the d-d transitions and the magnetic moment values of the complexes are given in Table 1. The Ni<sup>II</sup> complexes exhibit magnetic moment values of 2.90 and 2.88 BM, which correspond to two unpaired electrons, respectively.

<sup>\*</sup> Prof. Dr. O. Z. Yeşilel Fax: +90-222-2393578 E-Mail: yesilel@ogu.edu.tr

 <sup>[</sup>a] Faculty of Arts and Sciences, Department of Chemistry Eskişehir Osmangazi University 26480 Eskişehir, Turkey

<sup>[</sup>b] Faculty of Arts and Sciences, Department of Physics, Ondokuz Mayıs University, Samsun, Turkey

 Table 1. Electronic spectra and magnetic moment values of 1 and 2.

	1	2
$\frac{1}{\lambda_{\text{max}}}$ /nm	621	652
	884	895
$\varepsilon / L \cdot cm^{-1} \cdot mol^{-1}$	11	16
	6	13
Assignment of d-d transitions	${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$	${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$
-	${}^{3}A_{2\sigma} \rightarrow {}^{3}T_{2\sigma}$	${}^{3}A_{2\sigma} \rightarrow {}^{3}T_{2\sigma}$
$\Delta_{\rm o}$ /cm <sup>-1</sup>	11,300	11,230
$\mu_{\rm eff}$ /BM	2.90	2.88

**Table 2.** IR spectra of complexes<sup>a)</sup>  $/cm^{-1}$ .

Assignments	H <sub>3</sub> Or [23]	1	2
v <sub>OH</sub>	3241 sh	3383 s	_
V <sub>NH2</sub>	_	_	3447, 3415 s
V <sub>N(3)</sub> H	3154 m	3132 s	3280 s
VN(DH	3137 m	_	_
VCH	3099 s	3074 w	3157 m
V <sub>CH3</sub>	_	2853 w	2996, 2874 m
$v_{C=Oacid} + v_{C(2)=O}$	1729, 1719 vs	1636 vs, b	1653 vs
$v_{C(6)=0} + v_{ring}$	1700 vs	1636 vs, b	1623 vs
$v_{C=C} + v_{ring}$	1653 vs	1589 m	1568 sh
V <sub>C=N</sub>	1435 s	1472 m	1463 s

<sup>a)</sup> Abbreviations: w – weak; m – medium; s – strong; vs. – very strong, b – broad, sh – shoulder.

The electronic spectra of complexes **1** and **2** in H<sub>2</sub>O exhibit absorption bands at 621 ( $\varepsilon = 11 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), 652 ( $\varepsilon = 16 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) and 884 ( $\varepsilon = 6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), 895 nm ( $\varepsilon = 13 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), assigned to the  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$  and the  ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g} \text{ d} - \text{d}$  transitions, respectively. The  $\Delta_{0}$  value was calculated as 11300 for **1** and 11230 for **2** cm<sup>-1</sup> [22]. The absorption bands below 350 nm are due to intraligand transitions.

#### Infrared Spectra of 1 and 2

The most significant frequencies in the IR spectra of 1 and **2** are given in Table 2. The broad band at  $3383 \text{ cm}^{-1}$ is characteristic of water molecules involved in moderately strong hydrogen bonding. The observed NH<sub>2</sub> stretching frequencies in the region 3447 - 3415 cm<sup>-1</sup> clearly reveal the presence of dmpen ligand in 2. The bands at 3132 and  $3280 \text{ cm}^{-1}$  are attributed to the NH stretching vibration in the  $HOr^{2-}$  ligand for 1 and 2, respectively. The weak bands between 3074-2853 cm<sup>-1</sup> for 1 and 3157-2874 cm<sup>-1</sup> for 2 are due to the  $v_{(C-H)}$  vibrations. The position of carbonyl and carboxylate groups of orotate moiety can be used to characterize the coordination mode. The carbonyl stretching bands of the free orotic acid observed at 1729 and  $1719 \text{ cm}^{-1}$  ( $v_{C=O(acid)} + v_{C(2)=O}$ ) and at  $1700 \text{ cm}^{-1}$  $[v_{C(6)=O}+v_{ring}]$  [23]. These bands appear as strong broad bands at 1636  $\text{cm}^{-1}$ , as a broad band in 1, and at 1653 and  $1623 \text{ cm}^{-1}$  in **2**. These shifts indicate that the orotate ligands are coordinated as bidentate ligands. The bands with strong intensity around  $1575 \text{ cm}^{-1}$  correspond to the  $v_{(C=C)}$  vibrations of the pyrimidine ring of orotate, whereas the  $v_{(C=N)}$  vibrations are observed at approximately  $1466 \text{ cm}^{-1}$  in both complexes.

#### Thermal Analyses of 1 and 2

 $[Ni(HOr)(H_2O)_2(tmen)] \cdot H_2O(1)$ 

In the first stage, endothermic loss of crystal water occurs in the 65–135 °C temperature range (DTG<sub>max.</sub> = 107 °C, mass loss found 4.98 %, calcd. 4.71 %). The second stage [Ni(HOr)(H<sub>2</sub>O)<sub>2</sub>(tmen)] is related to the release of the aqua ligands between 148 and 233 °C (DTG<sub>max</sub> = 206 and 217 °C, mass loss found 8.98 %, calcd. 9.42 %). These stages show thermochromism, blue  $\rightarrow$  green. The anhydrous complex is rehydrated immediately after cooling in an open atmosphere. In the 234–421 °C temperature range, tmen and HOr ligands are lost in two endothermic steps. The following stage involves the burning of the organic residues (DTG<sub>max.</sub> = 519 °C), leading finally to NiO. The overall weight loss of 80.03 % (calcd. 80.49 %) agrees with the proposed pathway.

## $[Ni(HOr)(dmpen)_2]$ (2)

The complex is thermally stable up to about 285 °C. In the temperature range of 285-400 °C, the three stages of the Ni<sup>II</sup> complex are related to the successive decomposition of the neutral dmpen ligands and partial decomposition of orotates by giving exothermic contribution (DTA-max = 318, 377 and 400 °C. The final solid product of the thermal decomposition was identified as NiO. The total mass loss of the decomposition process was 84.05 % (calcd. 82.09 %).

Table 3. Crystal data and structure refinements for 1 and 2.

	1	2
Empirical formula	$NiC_{11}H_{22}O_6N_4 \cdot H_2O_6$	NiC15H30N6O4
Temperature /K	296 (2)	296 (2)
Crystal system	triclinic	monoclinic
Space group	$P\overline{1}$	$P2_1/c$
Unit cell dimensions		
a	8.491 (1)	10.086 (1)
b	10.206 (1)	18.667 (1)
c /Å	11.570 (1)	11.621 (1)
α	68.198 (5)	
β	70.022 (5)	118.171 (3)
γ /°	75.826 (5)	
$V/Å^3$	866.9 (1)	1928.6 (2)
Ζ	2	4
Absorption coefficient /mm <sup>-1</sup>	1.16	1.04
$D \text{calc} / \text{mg} \cdot \text{m}^{-3}$	1.467	1.437
Theta range for data	2.58-27.89	1.99 - 27.98
collection /°		
Measured reflections	18759	32322
Independent reflections	$4051 \ [R_{\rm int} = 0.043]$	$4579 [R_{int} = 0.053]$
$h \mid k \mid l$	11, 13, 15	13, 24, 15
Absorption correction		Integration X-RED
Refinement method		Integration
Final R indices $[F^2 > 2\sigma(F^2)]$	$R_1 = 0.052,$	$R_1 = 0.030,$
	$wR_2 = 0.152$	$wR_2 = 0.078$
Goodness-of-fit on F2	1.02	1.04
Largest difference peak and hole /e $\cdot {\rm \AA}^{-3}$	0.42; -0.50	0.28; -0.33



**Figure 1.** Ortep III view of **1** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. For clarity, only the major part of the disordered fragment is shown.

## Crystal Structures of 1 and 2

## $[Ni(HOr)(H_2O)_2(tmen)] \cdot H_2O$ (1)

The details of the crystal structure are given in Table 3. Selected bond lengths and angles are given in Table 4. The crystal structure of the complex is presented in Figure 1. In the structure two water molecules, the orotato dianion and tmen act as ligands, saturating the metal coordination

Table 4. Selected bond lengths /Å and angles /° for 1 and 2.

Compound 1			
Ni1-O3	2.026(1)	Nil-N1A	2.154(2)
Nil-N4	2.073(2)	Nil-N1B	2.154(2)
Nil-O1	2.106(1)	O3-C7	1.261(2)
Nil-O2	2.130(2)	O4-C7	1.234(2)
Ni1-N2B	2.144(2)	O5-C10	1.246(2)
Ni1-N2A	2.145(2)	O6-C11	1.251(2)
Compound 2			
Ni1-N3A	2.078(6)	Nil-N4B	2.170(4)
Nil-O4	2.082(1)	Ni1-N3B	2.193(9)
Nil-N5	2.084(1)	O1-C1	1.239(2)
Nil-N4A	2.089(3)	O2-C2	1.237(2)
Nil-N6	2.112(1)	O3-C5	1.233(2)
Nil-Nl	2.124(1)	O4-C5	1.269(2)
Compound 1			
O3-Ni1-N4	80.06(5)	O3-Ni1-O2	87.61(6)
O3-Ni1-O1	170.80(6)	N4-Ni1-N1A	96.72(9)
N4-Ni1-O1	92.20(6)	O3-Ni1-N2A	94.00(7)
O1-Ni1-N2A	93.64(8)	N4-Ni1-O2	91.93(6)
N4-Ni1-O1	92.20(6)	O1-Ni1-N1A	91.09(8)
O1-Ni1-O2	87.70(7)	N4-Ni1-N2A	173.99(7)
O3-Ni1-N1A	94.73(8)	O2-Nil-N2A	86.91(8)
O2-Nil-NIA	171.30(8)	N2A-Ni1-N1A	84.57(9)
Compound 2			
N3A-Ni1-O4	89.9(4)	N6-Ni1-N1	93.9(1)
N3A-Ni1-N5	93.5(4)	N3A-Ni1-N4B	84.6(2)
O4-Ni1-N5	175.0(1)	O4-Ni1-N4B	96.7(1)
N3A-Ni1-N4A	89.9(2)	N5-Ni1-N4B	87.4(1)
O4-Nil-N4A	83.0(1)	N4A-Nil-N4B	14.7(1)
N5-Nil-N4A	100.6(1)	N6-Nil-N4B	95.1(1)
N3A-Nil-N6	175.8(4)	N1-Ni1-N4B	169.6(1)
O4-N11-N6	86.0(1)	N3A - N1I - N3B	0.1(8)
N5-N1I-N6	90.7(1)	O4-N1I-N3B	89.8(5)
N4A - N11 - N6	88.8(1)	N5-N1I-N3B	93.5(5)
N3A-N1I-NI	86.1(1)	N4A - N11 - N3B	89.9(2)
04-N11-N1	/8.8(1)	N0 = N11 = N3B	1/3./(3)
NO = N11 = N1	9/./(1)	NI = NII = N3B	80.0(2)
N4A = N11 = N1	101.3(1)	N4B = N11 = N3B	84.6(2)



sphere. An additional uncoordinated water molecule is present in the structure. The Ni $-N_{tmen}$  bond lengths are 2.154(2) and 2.144(2) Å. The Ni $-N_{HOr}$  [2.073(2) Å] and Ni $-O_{HOr}$  [2.026(1) Å] bond lengths are noticeably longer than those found in [Ni(HOr)(H<sub>2</sub>O)(4-mim)<sub>3</sub>]<sub>2</sub>·5H<sub>2</sub>O [2.084(2) and 2.078(2) Å] [11] and [NiHOr(H<sub>2</sub>O)<sub>2</sub>(ata)<sub>2</sub>] [2.108(2) and 2.100(2) Å] [24], and somewhat shorter than the values reported for [Ni(HOr)(H<sub>2</sub>O)<sub>4</sub>]·H<sub>2</sub>O [25] [2.049(3) and 2.023(3) Å]. The orotato intraligand bond lengths are comparable with those in similar nickel complexes [11, 19, 24–26]. The discrepancy between the carboxylate C7–O3 [1.261(2) Å] and C7–O4 [1.234(2) Å] distances reflects the coordination as well as the participation in hydrogen bonding.

The details of hydrogen bonding are given in Table 5. Both water molecules (coordinated and uncoordinated) participate in hydrogen bonding of O···O type (ranging from 2.680 to 2.793 Å), whereas the orotato ligands are included in the hydrogen bonds of N···O type (2.859 (2) Å]. Each of the HOr ligand is doubly hydrogen-bonded to a corresponding HOr<sup>2–</sup> ligand. These DA:AD-type hydrogen bonds involve the pyrimidine carbonyl oxygen atom and the amide N–H group [N(3)···O(5)<sup>*i*</sup> 2.859(2) Å, H(3)···O(5)<sup>*i*</sup> 2.00 Å, N(3)–H(3)···O(5)<sup>*i*</sup> 174°; *i*: -x + 2, -y + 1, -z + 1]. A strong intramolecular hydrogen bond connects O1-H1A···O6 (2.630 (2)) and O7–H7A···O5 (2.702 (2) Å] (Figure 2).



Figure 2. Packing diagram of 1 viewed along [-100].

#### $[Ni(HOr)(dmpen)_2]$ (2)

The molecular structure is shown in Figure 3 and selected bond lengths and bond angles are given in Table 4. In the complex, the Ni<sup>II</sup> ion exhibits a distorted octahedral coordination defined by four nitrogen atoms from two chelating dmpen ligands together with the bidentate orotato ligand.

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D-H···A	<i>d</i> (D−H) /Å	<i>d</i> (H···A) /Å	<i>d</i> (D····A) /Å	<(DHA) /°	Graphset Descriptor
Complex 1					
N3-H3-05 <sup>i</sup>	0.86	2.00	2.859(2)	174	$R_2^2(8)$
O1-H1A···O6	0.77(4)	1.87(4)	2.630(2)	168(3)	<i>S</i> (6)
O1-H1B····O7 <sup>ii</sup>	0.85(3)	1.96(3)	2.793(3)	169(3)	$R_2^{-1}(6)$
O2-H2B····O7 <sup>ii</sup>	0.82(3)	2.00(3)	2.793(2)	163(3)	$\bar{R_2^{-1}(6)}$
O2-H2A····O4 <sup>iii</sup>	0.78(3)	1.91(3)	2.680(2)	174(3)	$R_2^{-2}(12)$
O7-H7A···O5	0.78(3)	1.97(3)	2.702(2)	157(3)	$R_{2}^{-4}(16)$
O7-H7B····O6 <sup>i</sup>	0.83(3)	1.93(3)	2.758(2)	170(3)	$R_2^{-4}(16)$
Symmetry codes: (i) -	-x + 2, -y + 1, -z +	1; (ii) x, y-1, z; (iii) -	-x + 2, -y + 1, -z.		
Complex 2					
N2-H2···O3 <sup>i</sup>	0.86	2.18	3.007(2)	162	C(7)
N5-H5A····O2 <sup>ii</sup>	0.90	2.19	2.970(2)	144	C(7)
N5-H5B····O1	0.90	2.11	2.912(2)	149	S(6)
Symmetry codes: (i) x	z, -y + 1/2, z + 1/2; (if	i) $x + 1$ , $-y + 1/2$ , $z + 1/2$	- 1/2.		

Table 5. Hydrogen-bonding lenghts and angles for 1 and 2.

The Ni–N3/N4/N5/N6 distances are different from each other and lie in a wide range [2.078(6)-2.193(9) Å]. The orotato ligand is coordinated to the Ni<sup>II</sup> ion through nitrogen and oxygen atoms [Ni1-O4 = 2.082(1) Å and Ni–N1 = 2.124(1) Å]. The angle O4–Ni1–N5  $[175.00(5)^{\circ}]$  is virtually linear, whereas N1–Ni1–N4  $[169.61(11)^{\circ}]$  and N4–Ni1–N1  $[161.29(11)^{\circ}]$  deviate much from linearity. On this basis, atoms O4, N1, N4 and N5 can be chosen to form the basal plane of the octahedron, and the equatorial positions are occupied by atoms N3 and N6. The equatorial plane and the orotato ligand are approximately planar. The Ni1–N1 and Ni1–O4 bond lengths are similar to that found in other Ni<sup>II</sup>-orotato complexes [11, 24, 25] and the angle of N1–Ni1–O4  $[78.77(5)^{\circ}]$  is nearly equal with previously reported complexes [11, 24, 25].



**Figure 3.** Ortep III view of **2** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. For clarity, only major part of disordered fragment is shown.

The crystal packing is stabilized by intra- and intermolecular hydrogen bonding between the N2–H2, N5–H5 atoms from dmpen and O1, O2, and O3 atoms form the orotato ligand [N2···O3<sup>*i*</sup> = 3.007(2), N5···O2<sup>*ii*</sup> = 2.970(2) and N5···O1 = 2.912(2) Å, (*i*) x, -y + 1/2, z + 1/2; (*ii*) x + 1, -y + 1/2, z + 1/2] (Figure 4).



Figure 4. Packing diagram of 2 viewed along [-100].

## **Experimental Section**

#### Materials and Measurements

All chemicals used were of analytical reagent grade and were commercially purchased. IR spectra were obtained with a Bruker Tensor 27 FT-IR spectrometer using KBr pellets in the  $4000-400 \text{ cm}^{-1}$  range. Elemental analyses for C, H and N were performed by using a Carlo Erba 1106 microanalyzer. Magnetic susceptibility measurements at room temperature were performed by using a Sherwood Scientific MXI model Gouy magnetic balance. The UV/Vis spectra were obtained for aqueous solutions of the complexes ( $10^{-3} \text{ M}$ ) with a Unicam UV2 spectrometer in the range 900–190 nm. A Perkin–Elmer Diamond TG/DTA Thermal Analyzer was used to record simultaneous TG, DTG and DTA curves in static air atmosphere at a heating rate of  $10 \, {}^{\circ}\text{C} \cdot \text{min}^{-1}$  in the temperature range 20-1000 °C using platinum crucibles.

#### Preparation of 1 and 2

A solution of tmen (0.58 g, 5 mmol) or dmpen (0.51 g, 5 mmol) in water (10 mL) was added dropwise with stirring to a solution of  $[Ni(HOr)(H_2O)_4]$ ·H<sub>2</sub>O [14] (0.76 g, 2.5 mmol) in distilled water (25 mL). The solutions were heated to 60 °C in a temperature-controlled bath and stirred for 5 h at 60 °C. Afterwards, the reaction mixtures were cooled to room temperature. The blue Ni<sup>II</sup> complex crystals were filtered and washed with cool distilled water (15 mL) and acetone, and dried in air. C11H24N4O7Ni (383.02): calculated C 34.49, H 6.32, N 14.63 %; found: C 34.42, H 6.33, N 14.76 %. C15H30N6O4Ni (417.13): calculated C 43.19, H 7.25, N 20.15 %; found: C 43.21, H 7.23, N 20.15 %.

#### Crystallographic Analysis

Single-crystal X-ray data were collected with a Stoe X-AREA single crystal diffractometer using monochromated  $MoK_{\alpha}$  radiation at 296 K. The structures were solved by direct methods and conventional Fourier methods. The program used for cell refinement was Stoe X-AREA [27], SHELXS-97 and SHELXL-97 [28] were used for solving and refining the structures. Molecular graphics: ORTEP-3 for Windows [29]. Software used to prepare material for publication: wingx [29] publication routines. Further details concerning data collection and refinement are given in Table 3.

Inspection of the displacement ellipsoids of tmen ligand in compound 1 and dmpen ligand in compound 2 shows a large anisotropy of the ligand atoms. This suggests that the two ligand atoms show positional disorder, therefore, a split model is necessary. The disordered atoms of the two ligands were modelled over two orientations and the refined site-occupancy factors of the disordered parts, viz, (N1A/N2A/C1A-C6A)/(N1B/N2B/C1B-C6B) and (N3A/N4A/C6A-C10A)/(N3B/N4B/C6B-C10B), are 0.679(3)/ 0.321(3) % and 0.572(3)/0.428(3) %, respectively. The disordered atoms were refined by using the following restraints: SIMU, DELU and SADI [28].

In compound 1, the five-membered chelate ring formed by atoms Ni1/O3/C7/C8/N4 is planar [maximum deviation -0.021(3) Å for atom N4], whereas the other five-membered chelate ring formed by atoms Ni1/N1/C3/C4/N2 is twisted on the C3-C4 bond with puckering parameters [30] of Q = 0.4560 Å and  $\varphi = 267.10^{\circ}$  for the atom sequence Ni1/N1A/C3A/C4A/N2A and with puckering parameters of O = 0.4466 Å and  $\varphi = 93.99^{\circ}$  for the atom sequence Ni1/N1B/C3B/C4B/N2B. In compound 2, the five-membered chelate ring formed by atoms Ni1/O4/C5/C4/N1 is planar [maximum deviation -0.038(3) Å for atom N1], whereas the two six-membered chelate rings formed by atoms Ni1/N3/C6/C7/C8/N4 and Ni1/N5/C11/C12/C13/N6 adopt a chair conformation as is evident from the puckering parameters: Q = 0.5598 Å,  $\theta = 12.36^{\circ}$  and  $\varphi =$ 185.17° for the atom sequence Ni1/N3A/C6A/C7A/C8A/N4A, Q =0.8396 Å,  $\theta = 93.61^{\circ}$  and  $\varphi = 101.47^{\circ}$  for the atom sequence Ni1/ N3B/C6B/C7B/C8B/N4B, and Q = 0.5280 Å,  $\theta = 158.75^{\circ}$  and  $\varphi =$ 

356.15° for the atom sequence Ni1/N5/C11/C12/C13/N6.

Crystallographic data for the structure reported here have been deposited (CCDC-638270 for 1 and -656858 for 2). Copies of the data can be obtained free of change from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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