New Pyridylene-bridged Bisoxazoles – Synthesis and Structural Study

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The bisoxazoles **1a** – **1c** that feature structures with two oxazole moieties connected to a 2,6-pyridylene central linker and contain different aryl substituents in 4- and 5-positions of the oxazole rings have been synthesized. Single-crystal X-ray structure determinations of the free ligand **1a**, containing the $NiCl_2$ complex of **1c** as the CH_3COOH solvate as well as the 1,4-dioxane-solvated diester intermediate **2a** are reported, which show specific molecular conformations and packings in the crystals. The conformation of **1a** is *syn* with reference to the oxazole nitrogen atoms and *anti* with reference to the oxazole and pyridine nitrogen atoms. In the Ni^{2+} complex, the metal ion is in an octahedral coordination environment with the nitrogens of **1c** and an oxygen of an acetic acid molecule in the basal plane, while two chloride ions occupy the axial positions of three additional acetic acid molecules one is hydrogen-bonded to a chloride and two form a carboxylic dimer, thus giving rise to a 1 : 1 : 4 (**1c** : $NiCl_2$: HOAc) stoichiometric ratio. The crystalline 1 : 1 inclusion compound of **2a** with 1,4-dioxane suggests a typical clathrate owing to the bulkyness of the host molecule.

Key words: Pyridine Derivatives, Oxazole Derivatives, Nickel, Coordination Compound, X-Ray Diffraction Analysis

Introduction

Aryl-substituted oxazoles are an interesting class of compounds due to their high fluorescence [1]. Owing to this property, some particular 2,5-diaryloxazoles have found commercial application as solutes in liquid scintillators [2] and as optical brightening agents [3]. A well-known compound of this type is 1,4-bis(5-phenyloxazol-2-yl)benzene, usually termed POPOP [4]. On the other side, analogous bis(benzoxazole)s featuring a 2,6-substituted pyridine ring as a linker between the benzoxazole moieties, thus corresponding to the tridentate 2,2′,6′,2″-terpyridine structure, have proven to be effective ligands for the complexation of Fe(II) and Zn(II) [5] or as receptors for dialkylammonium cations [6]. They have also been used for the separation of lanthanides and actinides [7], and as ancillary ligands for the formation of particular ruthenium [8] or model copper-dioxygen complexes [9]. However, as far as we know, bisoxazoles having a central 2,6-pyridylene bridge and aryl residues attached to the 4- and 5-positions of the oxazole units, such as illustrated in Scheme 1, are not documented in the literature. Only one special compound related to

|		
1 a	R = H
b	R = OCH_3
c	R = *t*-Bu
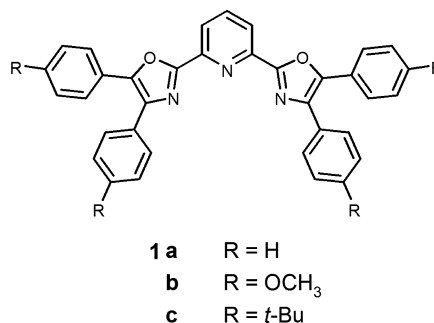
Scheme 1. The bisoxazoles studied in this paper.

this substance type is mentioned as a potential sensitizer in a recent patent [10].

Here we describe the synthesis of the bisoxazoles **1a** – **c** (Scheme 1) and report on the X-ray crystal structures of bisoxazole **1a**, the complex of **1c** with nickel(II) chloride and also the diester intermediate **2a**.

Results and Discussion

Compound preparation

Although there are different methods for the preparation of oxazoles in general [11, 12], only a very lim-
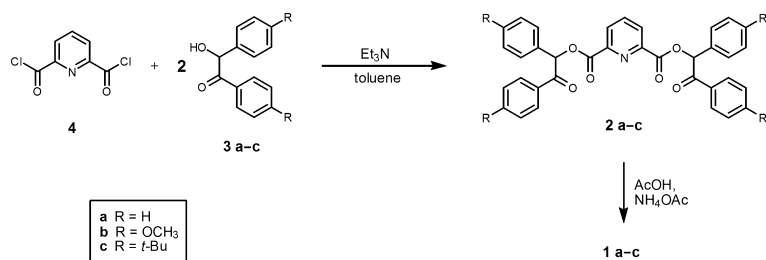
Scheme 2. Synthetic pathway for the preparation of the bisoxazoles.

ited number among them give potential access [13–15] to the compounds under consideration (Scheme 1). Perhaps the most promising one makes use of a ring condensation reaction between a 2-acyl ketone and ammonium acetate in acetic acid [16, 17], developed in close analogy to the Paal-Knorr cyclization [18]. Employment of the respective bis(ketoester)s **2a – c** under the mentioned conditions successfully indeed yielded the corresponding bisoxazoles **1a – c** (Scheme 2). The bis(ketoester)s **2a – c** were synthesized from benzoins **3a – c** and acid dichloride **4** following a procedure for related compounds [17]. The benzoins **3a – c** were obtained by the usual benzoin condensation [19] from the respective benzaldehyde. The Ni^{2+} complex of **1c**, [Ni(**1c**)Cl$_2$(HOAc)] · 3HOAc, was prepared from **1c** and NiCl$_2$ · 6H$_2$O in acetic acid, and the inclusion complex **2a** · 1,4-dioxane was obtained on crystallization of **2a** from this solvent.

X-Ray diffraction studies

The crystal structures of the compounds **1a**, **1c** · NiCl$_2$ · 4AcOH and **2a** · 1,4-dioxane (1 : 1), have been determined from single crystals in order to collect
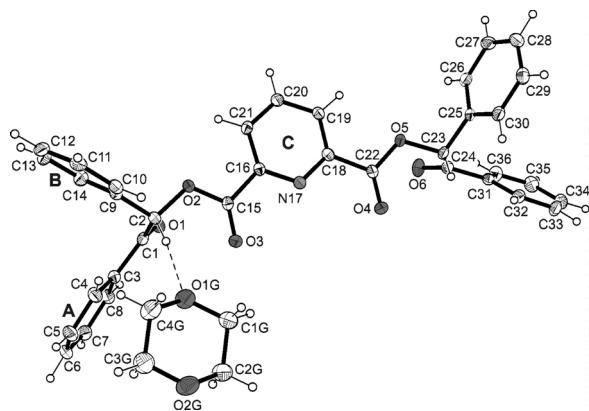

Fig. 1. Perspective view of **2a** · 1,4-dioxane (1 : 1), including numbering scheme of atoms and ring specification. Displacement ellipsoids are at the 50 % probability level.
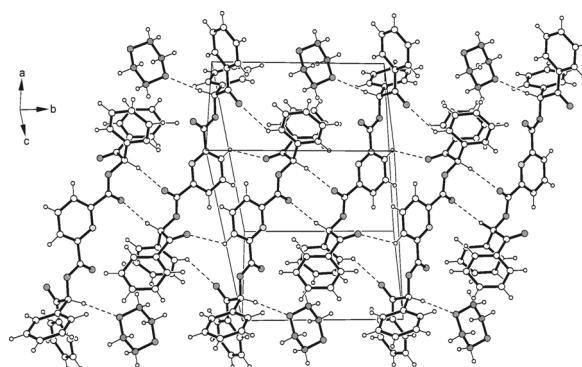

Fig. 2. Packing diagram of **2a** · 1,4-dioxane (1 : 1). Oxygen atoms are displayed as dotted, nitrogen atoms as hatched and carbon atoms of the guest molecules as grey circles. Broken lines represent hydrogen bond interactions.

information about the molecular structures and packing behavior of the various components in the solid state. Crystal and refinement data are summarized in Table 1. Perspective views of the molecular structures including the numbering schemes of atoms are shown in Figs. 1, 3 and 5. In order to simplify structural characterizations, the rings of the molecules are marked by capital letters in the illustrations of the molecular structures. Packing diagrams are presented in Figs. 2 and 4, while Fig. 6 presents the basic supramolecular unit of **1c**. Following the course of the synthesis, the structures of the compounds are described in the order **2a** · 1,4-dioxane (1 : 1), **1a** and **1c** · NiCl$_2$ · 4AcOH.

The 1 : 1 complex of the diester **2a** with 1,4-dioxane, the structure of which is displayed in Fig. 1, crystallizes as colorless plates in the space group $P\bar{1}$ with $Z = 2$. The two CO_2 fragments within the pyridine-2,6-dicarboxylate unit are twisted in the same direction at angles of 12.9(3) and 13.5(3)° with respect to the mean plane of the pyridine ring. The interplanar angles between the terminal phenyl rings are 84.0(1)° for the pair of rings A/B and 83.2(1)° for A'/B'. The torsion angles C(1)–C(2)–O(2)–C(15) and C(24)–C(23)–O(5)–C(22) are 73.3(2) and −79.8(2)°,
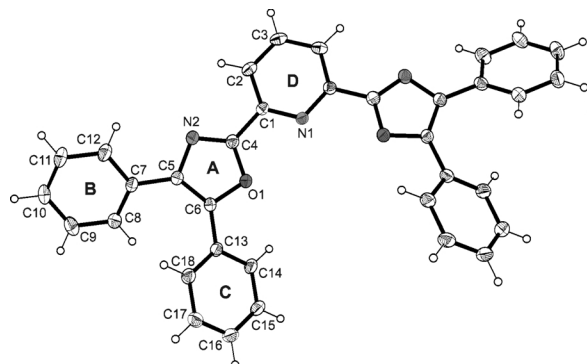
Fig. 3. Perspective view of **1a**, including numbering scheme of atoms and ring specification. Displacement ellipsoids are at the 50 % probability level.

respectively. Compound **2a** has opposite chirality at the stereogenic centers C(2) and C(23). This means, that under the given conditions of crystal growth only the *meso*-stereoisomer could be obtained in the crystalline state. Due to the inherent mirror symmetry of **2a**, the 1 : 1 stoichiometry of the complex of **2a** with 1,4-dioxane appears unusual as it implies an asymmetric binding behavior of the crystal components. The oxygen atom O(1G) of the solvent molecule is linked *via* a relatively strong C–H···O hydrogen bond [20] to the methine hydrogen H(2) [d(H···O) 2.40 Å], while the oxygen atom O(2G) acts as a bifurcated acceptor for a neighboring dioxane molecule [C(3G)–H(3G2)···O(2G) 2.61 Å, 158.5°] as well as to a further molecule of **2a** [C(28)–H(28)···O(2G) 2.61 Å, 152.2°]. Lacking conventional strong hydrogen bond donors [21], the host lattice is dominated by C–H···O=C interactions (Fig. 2) with H···O distances ranging between 2.44 – 2.71 Å. Contrary to expectations $\pi \cdots \pi$ stacking [22] is not observed.

Crystallization of the pyridine-linked bisoxazole **1a** from chloroform yields colorless crystals of the orthorhombic space group *Pbcn* with the asymmetric unit containing one half of the molecule. A perspective view of the molecule is presented in Fig. 3. The heterocyclic rings are inclined at an angle of 12.4(1)° with respect to the plane of the pyridine ring. The dihedral angle between the phenyl rings B and C is 41.1(1)°. Noteworthy, in the molecular structure of **1a**, the nitrogen of the pyridine is flanked by the oxygens of the oxazole rings. Moreover, neither the pyridine nor the oxazole heteroatoms are involved in hydrogen bond-type interactions. Instead, the packing of molecules is controlled by multiple arene interactions. They comprise C–H···π contacts [23] between peripheral aromatic
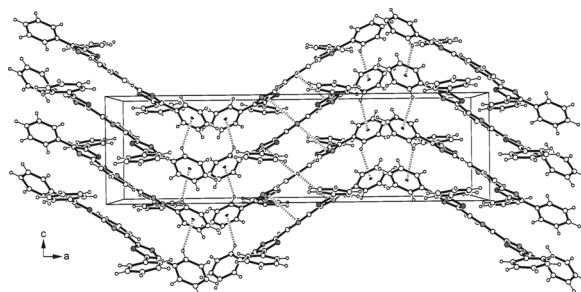

Fig. 4. Packing diagram of **1a** viewed along the crystallographic *b* axis. Broken double lines represent aromatic face-to-face interactions.

rings [C(12)–H(12)···*centroid*(B) 2.95 Å, 142.9°] and $\pi_{\text{pyridine}} \cdots \pi_{\text{oxazole}}$ interactions [24] with a distance of 3.54 Å between the centroids of interacting rings. As depicted in Fig. 4, the crystal structure of **1a** is constructed of molecular stacks extending in direction of the crystallographic *c* axis.

Crystallization of the *tert*-butyl-substituted bisoxazole **1c** from acetic acid in the presence of Ni(II) chloride, in the course of three month, yields green rods which turned out to be a complex of the composition [Ni(**1c**)Cl$_2$(HOAc)] · 3HOAc. A perspective view of the complex, which crystallizes in the space group $P\bar{1}$ with $Z = 2$, is illustrated in Fig. 5. The central tricyclic part of the complex ligand is approximately planar with largest atomic distances from the mean plane of this fragment being 0.093(1) for C(3) and −0.074(1) for C(16). As contrasted with **1a**, in the complex of

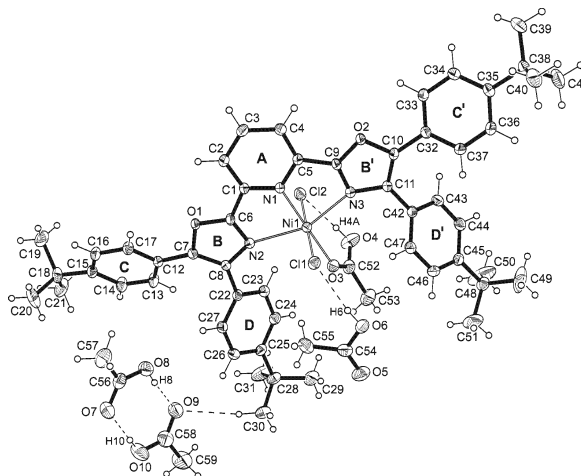Fig. 5. Perspective view of [Ni(**1c**)Cl$_2$(HOAc)] · 3HOAc, including numbering scheme of atoms and ring specification. Displacement ellipsoids are at the 50 % probability level. Thus lines represent coordinative bonds, broken lines hydrogen bond-type interactions.
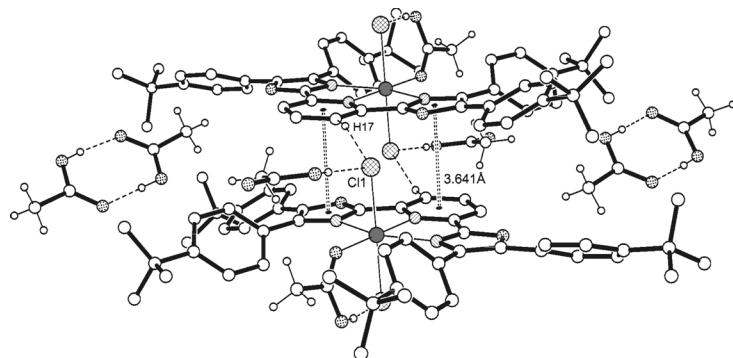
Fig. 6. Representation of the dimeric unit of the Ni(II) complex of **1c**. Hydrogen bond interactions are displayed as broken lines; broken double lines represent arene face-to-face interactions. Non-relevant hydrogen atoms of the bisoxazole molecules are omitted for clarity.

1c now the nitrogen atoms of the oxazoles are in *syn* orientation with reference to the nitrogen atom of the pyridine ring, thus giving rise to the geometry of a typical tridentate nitrogen donor ligand. The dihedral angles formed by the pairs of peripheric aromatic rings are 58.1(1) and 58.3(1)°.

The coordination environment of the nickel cation shows a distorted octahedral geometry of the type N_3OCl_2 with the nitrogens of the tridentate ligand and the oxygen of one molecule of acetic acid located in the equatorial plane, while the chloride ions occupy the axial positions of the polyhedron. The Ni–$N_{pyridine}$ distance is significantly shorter [2.041(1) Å] than the Ni–$N_{oxazole}$ distances [2.208(1), 2.277(1) Å]; the Ni–O distance is 2.066(1) Å, and the Ni–Cl bond lengths are 2.376(1) and 2.390(1) Å. The hydroxy hydrogen of the complexed acetic acid molecule is linked to one of the chloride anions by a strong hydrogen bond [O(4)–H(4)···Cl(2) 2.08 Å, 171.2°] [21], while the second chloride is associated with a further molecule of acetic acid [O(6)–H(6)···Cl(1) 2.28 Å, 172.2°]. The location of the methyl carbon of this solvent molecule near the aromatic ring B of the ligand [C(55)···*centroid*(B) 3.45 Å] indicates C–H···π(arene) bonding [23] which may also explain the unusual conformation of the acid molecule [C(55)–C(54)–O(6)–H(6) 3.0(2)°]. The remaining two molecules of acetic acid form a slightly distorted, non-centrosymmetric dimer [25] [O(8)–H(8)···O(9) 1.77 Å, 175.0°; O(10)–H(10)···O(7) 1.78 Å, 172.0°]. Dimeric units of the complex are formed by a relatively strong hydrogen bond between chloride Cl(1) and a pyridine hydrogen of a symmetry related complex molecule [26] [C(17)–H(17)···Cl(1) 2.69 Å, 164.4°] as well as by π···π interactions [24] with a distance of 3.614 Å between the centroids of pyridine and oxazole rings (Fig. 6). As the *tert*-butyl groups are located at the periphery of these dimeric units, only van der Waals forces exist between these large dimers.

Conclusions

The bisoxazoles **1a–c** featuring 2,6-pyridylene linkers between the oxazole moieties were synthesized in reasonable overall yields using a combination of esterification and ring condensation methods. With reference to the characteristic aryl substituents in the 4,5-positions of the oxazoles, they represent a new structural type of this particular compound class. As exemplary cases, the bis(oxazolyl)pyridine **1a**, the Ni^{2+} complex of **1c**, and the intermediate compound **2a**, have been studied with reference to their crystal structures, and the following features have emerged.

In the crystal structure of **1a**, the molecular conformation shows the nitrogen atom of the pyridine ring flanked by the oxygen atoms of the oxazoles, and the pyridine and oxazole units involved in intramolecular stacking contacts.

As was to be expected, in the Ni^{2+} complex of **1c** the nitrogen atoms of the oxazole rings and of the pyridine ring are all in *syn* conformation and coordinated to the Ni^{2+} ion. Thus **1c** behaves as a typical tridentate ligand, comparable with 2,2′,6′,2″-terpyridine [8] and related bisbenzoxazoles [5, 7]. However, unlike the usual complexes of these latter ligands, in the present case, the coordination octahedron can not be formed by using two of the bulkily substituted tridentate molecules **1c** for sterical reasons. Therefore, the three N donors of **1c** together with an oxygen atom of an acetic acid molecule are located in the equatorial plane, while two chloride ions occupy the axial positions of the coordination polyhedron. The second molecule of acetic acid is hydrogen-bonded to one of the chloride ions, and the remaining two acetic acid molecules form carb-

oxylic dimers that fill interstitial lattice space created in the packing of stacked complex dimers. Hence, on the one side, the bulky *p-tert*-butylphenyl substituents of **1c** prevent the common coordination mode of simple tridentate ligands and, on the other side, support lattice inclusion of solvent molecules [27] such as acetic acid in an unusually high 1:4 stoichiometric ratio.

Being in accordance with the construction principle of a bulkily substituted clathrate host [28], the crystalline diester intermediate **2a** also turned out to be a 1:1 stoichiometric inclusion compound with 1,4-dioxane. In this complex, the structure of **2a** shows a twisted conformation with reference to the aryl rings and a *meso* configuration regarding the methine stereogenic centers.

This latter property invites asking whether compounds of these structural types permit a development of a new class of clathrate hosts in general, capable of a variety of inclusions [27, 28]. *E. g.*, structural modification of the aryl substituents of these bisoxazoles can lead to a tailored selectively in the complexation of particular metal cations such as lanthanides and actinides [7] or dialkylammonium cations [6], which may then allow specific separations *via* extraction processes [29]. In this frame, the extraction of Am(III) and Ln(III) is mentioned as an important part of the processing of nuclear fuel [30]. It is also an interesting aspect to study potential conditions where the oxazoles tend to use the oxygen instead of the nitrogen atoms as donors. Moreover, the compounds are promising for their use as optical brightening agents [3] or as building blocks for light-emitting devices [31].

Experimental Section

General

Melting points: Kofler melting point microscope (uncorrected). IR: Nicolet FT-IR 510. ^{1}H and ^{13}C NMR (chemical shifts δ in ppm *vs.* TMS as internal standard): Bruker Avance DPX 400. MS (ESI): Quattro-LC (positive ion) and Esquire-LC (solvent: chloroform). Elemental analysis: Heraeus CHN rapid analyzer. TLC analysis: aluminum sheets precoated with silica gel 60 F$_{254}$ (Merck). Toluene was dried over sodium and freshly distilled before use. Triethylamine was dried over potassium hydroxide.

The starting benzoins **3a** [32], **3b** [33] and **3c** [34] were synthesized *via* benzoin condensation from the corresponding benzaldehydes following the described procedures. The 2,6-pyridinedicarbonyl dichloride (**4**) was prepared form 2,6-pyridinedicarboxylic acid and thionyl chloride according to the literature method [35]. 2,6-Pyridinedicarboxylic acid and other common reagents were purchased from commercial sources.

Preparation of bis(keto ester)s *2a* – *c*

General procedure

To a refluxing solution of the corresponding benzoin **3a** – **c** (20 mmol) and 2,6-pyridinedicarbonyl dichloride (**4**) (2.04 g, 10 mmol) in dry toluene (20 mL), triethylamine (15 mL, 0.11 mol) was slowly added during 3 h. After evaporation of the solvent, ethanol (10 mL) was added to the oily residue and the mixture stirred for 2 h. The solid which was formed was collected and crystallized. Details for the individual compounds are given below.

2a: Compound **3a** (4.24 g) was reacted. Crystallization from 1,4-dioxane yielded 2.45 g (44 %) of colorless crystals; m. p. 151 °C. – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.13 (s, 2 H, CH), 7.35 – 7.44 (m, 10 H, Ar-H), 7.51 – 7.60 (m, 6 H, Ar-H), 7.99 – 8.02 (m, 5 H, Ar-H), 8.35 (d, J_{HH} = 8.0 Hz, 2 H, Ar-H). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 79.1, 128.5, 128.6, 128.7, 28.9, 129.1, 129.3, 133.2, 133.5, 134.5, 138.2, 147.9, 163.6, 193.2. – IR (KBr): ν = 3065, 2980, 2944, 1752, 1727, 1699, 1599, 1581, 1235, 1146, 760, 696 cm^{-1}. – MS (ESI): *m/z* = 556 (calcd. 556.4 for C$_{35}$H$_{25}$NO$_6$, [M]$^+$). – Analysis for C$_{35}$H$_{25}$NO$_6 \cdot$ H$_2$O (573.60): calcd. C 73.29, H 4.74, N 2.44; found C 73.51, H 4.81, N 2.80.

2b: Compound **3b** (5.45 g) was reacted. Crystallization from ethanol yielded 4.94 g (73 %) of a brownish powder; m. p. 214 – 216 °C. – ^{1}H NMR (400 MHz, CDCl$_3$, [D$_6$]DMSO): δ = 3.78, 3.84, (2 s, 12 H, CH$_3$), 6.89 – 6.95 (m, 8 H, Ar-H), 7.14 (s, 2 H, CH), 7.51 (d, $^3J_{HH}$ = 8.4 Hz, 4 H, Ar-H), 8.02 (d, $^3J_{HH}$ = 8.8 Hz, 4 H, Ar-H), 8.13 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, Ar-H), 8.33 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, Ar-H). – ^{13}C NMR (100 MHz, CDCl$_3$ [D$_6$]DMSO): δ = 53.8, 54.1, 76.8, 112.6, 113.0, 124.1, 125.6, 128.8, 129.7, 137.3, 146.4, 158.8, 162.0, 162.0, 162.3, 190.0. – IR (KBr): ν = 3079, 2962, 2937, 2840, 1727, 1681, 1631, 1599, 1517, 1265, 1242, 1171, 1146 cm^{-1}. – MS (ESI): *m/z* = 676.4 (calcd. 676.2 for C$_{39}$H$_{33}$NO$_{10}$, [M+H]$^+$). – Analysis for C$_{39}$H$_{33}$NO$_{10}$ (675.21): calcd. C 69.33, H 4.92, N 2.07; found C 69.69, H 5.00, N 2.20.

2c: Compound **3c** (6.44 g) was reacted. Crystallization from 1,4-dioxane yielded 6.7 g (86 %) of a colorless powder; m. p. 182 °C. – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.28, 1.29 (2 s, 36 H, CH$_3$), 7.11 (s, 2 H, CH), 7.40, 7.43 (2d, $^3J_{HH}$ = 8.4 Hz, 8 H, Ar-H), 7.54 (d, $^3J_{HH}$ = 8.4 Hz, 4 H, Ar-H), 7.94 – 8.00 (m, 5 H, Ar-H), 8.34 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, Ar-H). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 31.0, 31.2, 34.7, 35.1, 78.7, 125.6, 126.1, 128.3, 128.4, 129.0, 130.6, 132.0, 138.0, 148.2, 152.4, 157.3, 163.6, 192.7. – IR (KBr): ν = 3090, 3062, 3030, 2962, 2905, 2865, 1751, 1730, 1695, 1602, 1233, 1141 cm^{-1}. – MS (ESI): *m/z* = 780 (calcd. 780.69 for C$_{51}$H$_{57}$NO$_6$, [M]$^+$). – Analysis for C$_{51}$H$_{57}$NO$_6 \cdot$ 0.5 H$_2$O

Table 1. Crystal data and parameters pertinent to data collection and structure refinement of **1a**, [Ni(**1c**)Cl$_2$(HOAc)] · 3HOAc and **2a**.

Compound	**1a**	[Ni(**1c**)Cl$_2$(HOAc)] · 3HOAc	**2a**
Empirical formula	C$_{35}$H$_{23}$N$_3$O$_2$	C$_{51}$H$_{55}$N$_3$O$_2$Cl$_2$Ni · 4 C$_2$H$_4$O$_2$	C$_{35}$H$_{25}$NO$_6$ · C$_4$H$_8$O$_2$
Formula weight, g mol^{-1}	517.56	1111.80	643.66
Crystal data			
Crystal system	orthorhombic	triclinic	triclinic
Space group	*Pbcn*	*P*$\bar{1}$	*P*$\bar{1}$
a, Å	30.1367(6)	13.156(2)	9.2390(3)
b, Å	10.1127(2)	13.369(3)	10.7711(4)
c, Å	8.4746(2)	16.826(3)	17.0938(6)
α, deg	90	96.367(6)	80.771(3)
β, deg	90	99.817(5)	77.743(2)
γ, deg	90	96.344(6)	86.650(3)
V, Å^3	2582.75(9)	2872.6(9)	1640.26(10)
Z	4	2	2
F(000), e	1080	1176	676
D_{calcd}, Mg m^{-3}	1.33	1.29	1.30
μ(MoK_α), mm^{-1}	0.1	0.5	0.1
Data collection			
Temperature, K	133(2)	153(2)	93(2)
θ limits, deg	1.3 – 29.1	2.4 – 30.1	2.3 – 29.4
Index ranges *hkl*	−41/41, −13/11, −11/11	−18/18, −18/18, −23/23	−12/12, −14/14, −23/23
No. of coll. / unique refl. / R_{int}	28675 / 3457 / 0.0271	46707 / 16867 / 0.0700	34925 / 8937 / 0.0825
No. of refl. with [$I \geq 2\,\sigma(I)$]	2957	11213	4788
Refinement			
No. of refined parameters	182	715	433
R1 (*F*) / *w*R2 (F^2)$^{a, b}$	0.0442 / 0.1507	0.0385 / 0.0956	0.0526 / 0.1516
Weighting scheme *x* / *y*^{b}	0.0806 / 0.8470	0.0391 / 0.0	0.0631 / 0.8486
S (Goodness of fit on F^2)^c	1.070	0.972	0.923
Final $\Delta\rho_{max/min}$, e Å^{-3}	0.38 / −0.32	0.52 / −0.39	0.34 / −0.27

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^{c} GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

(788.43): calcd. C 77.63, H 7.41, N 1.78; found C 77.50, H 7.50, N 2.02.

Preparation of bisoxazoles **1a** – **c**

General procedure

The corresponding bis(ketoester)s **2a** – **c** (7.5 mmol) and ammonium acetate (3.46 g, 45 mmol) were dissolved in conc. acetic acid (55.0 mL) and refluxed for 3.5 h. Work-up of the reaction mixture, purification methods and other details for the individual compounds are given below.

1a: Compound **2a** (4.17 g) was used for the reaction. The hot reaction mixture was poured into ice (150 mL) and neutralized with aqueous ammonia. The precipitate which was formed was collected, washed several times with water and dried. Crystallization from 1,4-dioxane yielded 1.0 g (26 %) of colorless crystals; m. p. 215 – 218 °C. – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.35 – 7.43 (m, 12 H, Ar-H), 7.75 – 7.78 (m, 8 H, Ar-H), 7.97 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, Ar-H), 8.30 (d, $^3J_{HH}$ = 7.9 Hz, 2 H, Ar-H). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 123.1, 127.2, 128.1, 128.3, 128.6, 128.6, 128.9, 132.1, 137.2, 137.8, 146.4, 147.3, 158.5. –

IR (KBr): ν = 3051, 3033, 1677, 1606, 1592, 1502, 1028 cm^{-1}. – MS (ESI): *m/z* = 518 (calcd. 518.0 for C$_{35}$H$_{23}$N$_3$O$_2$, [M]$^+$). – Analysis for C$_{35}$H$_{23}$N$_3$O$_2$ · 0.5 H$_2$O (526.77): calcd. C 79.83, H 4.59, N 7.98; found C 79.68, H 4.97, N 8.36.

1b: Compound **2b** (5.06 g) was used for the reaction. After cooling the reaction mixture to r. t., water (55 mL) was added followed by aqueous sodium hydrogen carbonate for neutralization. The organic layer was separated, washed with water and treated with *n*-hexane to form a solid. Crystallization from 1,4-dioxane yielded 1.15 g (24 %) of a pale-yellow powder; m. p. 68 °C. – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.83 (s, 12 H, CH$_3$), 6.87 – 6.97 (m, 10 H, Ar-H), 7.48 – 7.56 (m, 9 H, Ar-H). – ^{13}C NMR (100 MHz, DCCl$_3$): δ = 55.3, 55.3, 114.0, 114.1, 121.0, 125.2, 127.9, 129.0, 132.4, 133.8, 144.6, 159.3, 159.6. – IR (KBr): ν = 3047, 2997, 2958, 2930, 2833, 1590, 1520, 1498, 1251, 1034, 833 cm^{-1}. – MS (ESI): *m/z* = 638 (calcd. 638.0 for C$_{39}$H$_{31}$N$_3$O$_6$, [M]$^+$). – Analysis for C$_{39}$H$_{31}$N$_3$O$_6$ · 3.5 H$_2$O (700.92): calcd. C 66.83, H 5.46, N 6.02; found C 66.66, H 5.26, N 6.01.

1c: Compound **2c** (5.84 g) was used for the reaction. After cooling of the reaction mixture to r. t., the precipitate

which was formed was collected, neutralized with aqueous sodium hydrogen carbonate, washed several times with water and dried. Crystallization from 1,4-dioxane yielded 4.33 g (78 %) of a colorless powder; m. p. 315 °C. – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.33 (s, 36 H, CH$_3$), 7.44 (d, $^3J_{HH}$ = 8.4 Hz, 8 H, Ar-H), 7.72 – 7.76 (m, 8 H, Ar-H), 7.96 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar-H), 8.29 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, Ar-H). – ^{13}C NMR (100 MHz, DCCl$_3$): δ = 31.2, 31.3, 34.7, 34.8, 123.0, 125.5, 125.6, 125.7, 126.0, 126.8, 127.8, 129.5, 136.8, 137.6, 146.6, 147.2, 151.3, 152.1, 158.3. – IR (KBr): ν = 3087, 3069, 3037, 2962, 2905, 2869, 1627, 1570, 1495, 1267, 839 cm^{-1}. – MS (ESI): *m/z* = 742 (calcd. 742.5 for C$_{51}$H$_{55}$N$_3$O$_2$, [M]$^+$. – Analysis for C$_{51}$H$_{55}$N$_3$O$_2$ · 0.5 H$_2$O (751.20): calcd. C 81.54, H 7.51, N 5.62; found C 81.07, H 7.47, N 5.54.

X-Ray structure determinations

Single crystals of **1a** were grown by slow isothermal evaporation of saturated solutions in chloroform, **2a** · 1,4-dioxane on crystallization of **2a** from 1,4-dioxane. Single crystals of the metal complex [Ni(**1c**)Cl$_2$(HOAc)] · 3HOAc were obtained by isothermal evaporation of a saturated solution of **1c** and nickel(II) chloride in acetic acid. The intensity data were collected on a Bruker APEX II diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) using ω and ϕ scans. Reflections were corrected for background, Lorentz and polarization effects. Preliminary structure models were derived by application of Direct Methods [36], and the structures were refined by full-matrix least-squares calculation based on F^2 for all reflections [36]. With the exception of H(8) and H(10) in the structure of [Ni(**1c**)Cl$_2$(HOAc)] · 3HOAc, all other hydrogen atoms were included in the models in calculated positions and were refined as constrained to the bonding atoms.

The crystal data and parameters pertinent to data collection and structure refinement of the compounds studied are summarized in Table 1.

Supplementary material

CCDC 781694, 781695 and 781696 contain the crystallographic data for **1a**, [Ni(**1c**)Cl$_2$(HOAc)] · 3 HOAc and **2a**, respectively. These data can be obtained free of charge from the Cambrigde Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Further details on the crystal structures, including tables of structure parameters and geometric parameters for non-covalent contacts are given as Supplementary Material available online (www.znaturforsch.com/ab/v66b/c66b.htm).

[1] R. H. Wiley, *Chem. Rev.* **1945**, *37*, 401 – 442.
[2] C. G. Bell, F. N. Hayes (Eds.), *Liquid Scintillation Counting*, Pergamon, New York, **1958**.
[3] E. Schinzel, H. Frischkorn, T. Martini, EP 0106916, **1987**.
[4] F. N. Hayes, B. S. Rogers, D. G. Ott, *J. Am. Chem. Soc.* **1955**, *77*, 1850 – 1852.
[5] S. Rüttimann, C. M. Moreau, A. F. Williams, G. Bernardinelli, A. W. Addison, *Polyhedron* **1992**, *11*, 635 – 646.
[6] T. Suzuki, K. Sada, Y. Tateishi, T. Tani, S. Shinkai, *Tetrahedron Lett.* **2004**, *45*, 8161 – 8163.
[7] M. G. B. Drew, C. Hill, M. J. Hudson, P. B. Iveson, C. Madic, L. Vaillant, T. G. A. Youngs, *New. J. Chem.* **2004**, *28*, 462 – 470.
[8] A. Singh, G. Das, B. Mondal, *Polyhedron* **2008**, *27*, 2563 – 2568.
[9] C. Piguet, B. Bocquet, E. Müller, A. F. Williams, *Helv. Chim. Acta* **1989**, *72*, 323 – 337.
[10] B. Strehmel, H. Baumann, U. Dwars, D. Pietsch, A. Draber, M. Mursal, DE 022137B3, **2005**.
[11] I. J. Turchi (Ed.), *The Chemistry of Heterocyclic Compounds*, Wiley, New York, **1986**, Vol. 45.
[12] S. Lang-Fugmann, in *Methoden der Organischen Chemie*, (Houben-Weyl) Vol. E8a, (Ed.: E. Schaumann), Thieme, Stuttgart, **1994**, pp. 891 – 1019.
[13] J. C. Lee, H. J. Choi, Y. C. Lee, *Tetrahedron Lett.* **2003**, *44*, 123 – 125.
[14] A. R. Katritzky, Z. Wang, C. D. Hall, N. G. Akhmedov, A. A. Shestopalov, P. J. Steel, *J. Org. Chem.* **2003**, *68*, 9093 – 9099.
[15] J. R. Davies, P. D. Kane, C. J. Moody, *Tetrahedron* **2004**, *60*, 3967 – 3977.
[16] A. de Groot, H. Wynberg, *J. Org. Chem.* **1966**, *31*, 3954 – 3958.
[17] J. Heinze, DE 2731457, **1979**; *Chem. Abstr.* **1979**, *90*, 152164c.
[18] R. P. Bean, in *The Chemistry of Pyrroles*, Vol. 48/1, (Ed.: R. A. Jones), Wiley, New York, **1990**, pp. 206 – 220.
[19] W. S. Ide, J. S. Buck, *Org. React.* **1948**, *4*, 269 – 304.
[20] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond*, IUCr Monographs on Crystallography, Vol. 9, Oxford University Press, Oxford, **1999**.
[21] G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, **1997**, pp. 33 – 55.
[22] I. A. Dance, in *Encyclopedia of Supramolecular Chemistry*, (Eds.: J. L. Atwood, J. W. Steed), CRC Press, Boca Raton, **2004**, pp. 1076 – 1092.
[23] M. Nishio, *CrystEngComm* **2004**, *6*, 130 – 158.
[24] S. M. M. Sony, M. N. Ponnuswamy, *Cryst. Growth Des.* **2006**, *6*, 736 – 742.

[25] I. Csöregh, M. Czugler, E. Weber, J. Ahrendt, *J. Incl. Phenom.* **1990**, *8*, 309 – 322.

[26] D. Yoon, D. E. Gross, V. M. Lynch, J. L. Sessler, B. P. Hay, C. Lee, *Angew. Chem.* **2008**, *120*, 5116 – 5120; *Angew. Chem. Int. Ed.* **2008**, *47*, 5038 – 5042.

[27] A. Nangia, in *Nanoporous Materials*, Series on Chemical Engineering, Vol. 4, (Eds.: G. Q. Lu, X. S. Zhao), Imperial College Press, London, **2004**, pp. 165 – 187.

[28] E. Weber, in *Comprehensive Supramolecular Chemistry*, Vol. 6, (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Elsevier Science, Oxford, **1996**, pp. 535 – 592.

[29] M. J. Hudson, M. G. B. Drew, M. R. S. Foreman, C. Hill, N. Huet, C. Madic, T. G. A. Youngs, *Dalton Trans.* **2003**, 1675 – 1685.

[30] J. N. Mathur, M. S. Murali, K. L. Nash, *Solv. Extr. Ion Exch.* **2001**, 237 – 390.

[31] T. S. Kim, T. Okubo, T. Mitani, *Chem. Mater.* **2003**, *15*, 4949 – 4955.

[32] A. Breuer, T. Zincke, *Liebigs Ann. Chem.* **1879**, *198*, 141 – 190.

[33] G. Sumrell, J. I. Stevens, G. E. Goheen, *J. Org. Chem.* **1957**, *22*, 39 – 41.

[34] B. Hahn, B. Köpke, J. Voß, *Liebigs Ann. Chem.* **1981**, 10 – 19.

[35] W. Ried, G. Neidhardt, *Liebigs Ann. Chem.* **1963**, *666*, 148 – 155.

[36] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467 – 473; *ibid.* **2008**, *A64*, 112 – 122.

New Pyridylene Bridged Oxazoles – Synthesis and Structural Study

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Supplementary Material

Table S1. Interplanar angles (°) of aromatic units in the compounds studied.

Compound	1a	[Ni(1c)Cl$_2$(HOAc)] · 3HOAc	2a
Interplanar angles			
A/B	25.2(1)	44.9(1)	
A'/B'		48.9(1)	
A/C	32.0(1)	22.9(1)	85.0(1)
A'/C'		24.5(1)	64.9(1)
A/D	12.4(1)	6.9(1)	
A'/D		2.5(1)	
B/C	41.1(1)	58.1(1)	82.7(1)
B'/C'		58.3(1)	58.2(1)

Table S2. Geometric parameters of the Ni(II) involved interactions in

[Ni(1c)Cl$_2$(HOAc)] · 3HOAc.

Bond lengths (Å)		Bond angles (°)	
Ni(1)–N(1)	2.277(1)	N(1)–Ni(1)–N(3)	154.0(1)
Ni(1)–N(2)	2.041(1)	N(2)–Ni(1)–O(3)	179.6(1)
Ni(1)–N(3)	2.208(1)	Cl(1)–Ni(1)–Cl(2)	179.5(1)
Ni(1)–O(3)	2.066(1)		
Ni(1)–Cl(1)	2.376(1)		
Ni(1)–Cl(2)	2.390(1)		

Table S3. Geometric parameters for non-covalent contacts in the compounds studied.

Atoms involved	Symmetry	Distance (Å)		Angle (°)
D–H⋯A		D⋯A	H⋯A	D–H⋯A

1a

C(12)–H(12)⋯*centroid*(ring B)[a]	x, −y, 0.5+z	3.756(3)	2.95	143

[Ni(**1c**)Cl$_2$(HOAc)]·3HOAc

O(4)–H(4)⋯Cl(2)	x, y, z	2.917(2)	2.08	171
O(6)–H(6)⋯Cl(1)	x, y, z	3.116(2)	2.28	172
C(17)–H(17)⋯Cl(1)	1−x, 1−y, 1−z	3.616(2)	2.69	164
O(8)–H(8)⋯O(9)	x, y, z	2.613(2)	1.77	175
O(10)–H(10)⋯O(7)	x, y, z	2.632(2)	1.78	172
C(19)–H(19)⋯O(5)	1+x, y, z	3.303(2)	2.66	125
C(28)–H(28)⋯O(7)	−x, 1−y, 1−z	3.540(2)	2.73	144
C(51)–H(51B)⋯O(10)	1+x, −1+y, 1+−z	3.626(2)	2.66	166
C(55)–H(55B)⋯*centroid*(ring B)[a]	1−x, 1−y, 1−z	3.447(3)	2.89	117.1
C(57)–H(57B)⋯*centroid*(ring C)[a]	x, y, z	3.802(3)	2.84	166
C(43A)–H(43E)⋯C(3)[b]	1−x, 2−y, 1−z	3.405(3)	2.59	139

2a

C(26)–H(26)⋯O(1)	1−x, 2−y, 1−z	3.213(3)	2.54	128
C(11)–H(11)⋯O(3)	1−x, y, z	3.466(3)	2.71	137
C(6)–H(6)⋯O(3)	2−x, 2−y, −z	3.327(3)	2.63	130
C(23)–H(23)⋯O(4)	1−x, 1−y, 1−z	3.364(3)	2.52	142

C(34)–H(34)···O(4)	–x, 1–y, 1–z	3.112(3)	2.47	124
C(21)–H(21)···O(6)	–1+x, y, z	2.956(3)	2.44	114
C(2)–H(2)···O(1G)	1+x, y, z	3.394(3)	2.40	173
C(28)–H(28)···O(2G)	x, y, 1+z	3.481(3)	2.61	152
C(3G)–H(3G2)···O(2G)	1–x, 1–y, –z	3.552(3)	2.61	158

[a] Means centre of the aromatic ring. Ring B: C(4)…C(9), ring C: C(10)…C(15), ring B':
C(25)…C(30), ring C': C(31)…C(36).

[b] To achieve a reasonable hydrogen bond geometry, an individual atom instead the ring
centroid was chosen as acceptor