

69. Syntheses and Crystal Structures of 4,5-Dihydro-2-(2'-hydroxyphenyl)oxazole-Containing Metal Complexes

by Carsten Bolm* and Konrad Weickhardt¹⁾

Institut für Organische Chemie der Universität Basel, St. Johannis-Ring 19, CH-4056 Basel

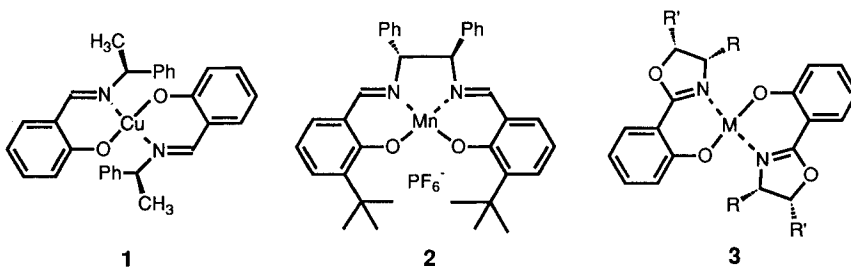
and Margareta Zehnder and Dorothea Glasmacher²⁾

Institut für Anorganische Chemie der Universität Basel, Spitalstrasse 51, CH-4056 Basel

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The synthesis of the complexes **3** of various metals ligated to chiral 4,5-dihydro-2-(2'-oxidophenyl- κO)oxazoles- κN is described (*Scheme*). Three of them, i.e. **3a**, **3e**, and **3f** containing Cu^{II}, Zn^{II}, and Ni^{II}, respectively, were analyzed by X-ray diffraction studies. A series of Cu^{II} complexes (**6a–d**) with differently substituted dihydrooxazoles have been synthesized.

1. Introduction. – In 1966, Nozaki *et al.* described the asymmetric cyclopropane formation catalyzed by the (salicylaldiminato)copper(II) complex **1** (salicylaldiminato ligand = [C-(2-oxidophenyl- κO)methanimine- κN]) [1]. This was one of the first enantioselective chemical transformations using catalytic amounts of homogeneous chiral metal complexes. Since then, a large number of efficient metal catalysts with bi- or multidentate *Schiff* bases, derived from substituted salicylaldimine derivatives, were developed. Modifications of the ligand led to high enantioselectivities in a variety of



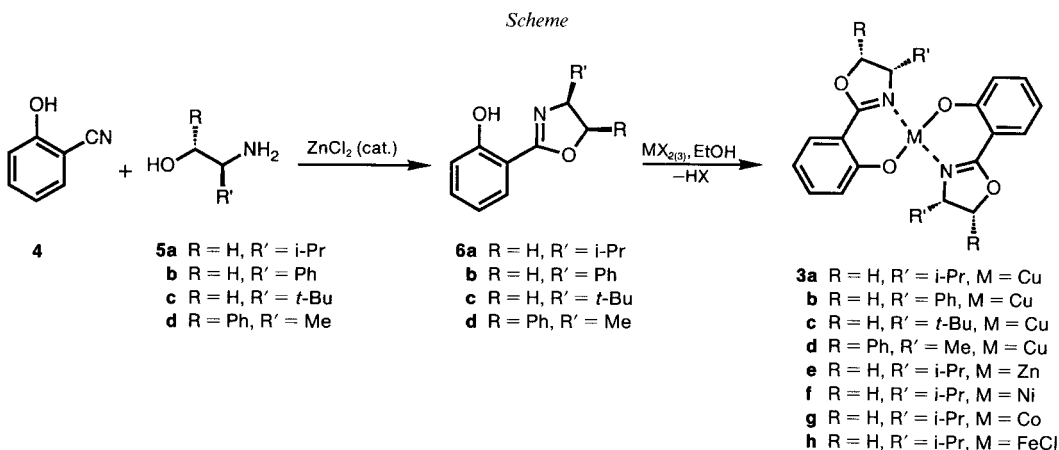
reactions. *E.g.*, optically active Cu^{II} complexes were used in the synthesis of cyclopropanes [2], asymmetric epoxidation of simple alkenes was achieved with (salen)manganese complex **2** [3], and enantioselective cyclization was catalyzed by an analogous (salen)cobalt complex [4]. The general concept is based on the conformational rigidity induced by the metal–N bonds which creates an appropriate three-dimensional structure for chiral recognition of the substrate.

¹⁾ Part of the projected Ph. D. thesis, Universität Basel.

²⁾ Visiting student from the Technische Hochschule Aachen, Germany.

During our studies of new ligands for enantioselective catalysis [5], we have developed a facile synthesis of 4,5-dihydro-2-(2'-hydroxyphenyl)oxazoles [6]. Derivatives of this kind serve as chelating units in microbial metal-transporting agents which show high affinity and specificity for Fe^{III} [7]. In contrast to the great number of structural investigations of (salicylaldiminato)metal complexes, the corresponding 4,5-dihydrooxazole-containing compounds **3** have been rather neglected. This is even more surprising, considering the fact that other (4,5-dihydrooxazole)metal complexes have recently been shown to be efficient catalysts in asymmetric processes [8]. To investigate these species, we have synthesized several metal complexes and studied their properties and structures in solution and in the solid state.

2. Results and Discussion. – 2.1. *Synthesis.* The 2-hydroxybenzonitrile (**4**) reacts with enantiomerically pure aminoalcohols **5a–d** under ZnCl_2 catalysis to give the corresponding optically active 4,5-dihydro-2-(2'-hydroxyphenyl)oxazoles **6a–d** (Scheme) [6]. Mono-



and disubstituted derivatives are obtained in high yield. Treatment of an EtOH solution of **6** with a solution of the metal salt MX_2 or MX_3 ($\text{X} = \text{OAc}$ or Cl) in EtOH results in either immediate precipitation of the metal complex [9], or crystals are obtained by slow evaporation of the solvent. The air-stable crystals $[\text{ML}_2]$ are collected by filtration and can be recrystallized from EtOH. Complexes of Cu^{II} (**3a**), Zn^{II} (**3e**), Ni^{II} (**3f**), Co^{II} (**3g**), and Fe^{III} (**3h**) derived from 4,5-dihydro-2-(2'-hydroxyphenyl)oxazole **6a** and the corresponding metal salt were synthesized and characterized by elemental analysis, NMR, IR, and UV spectroscopy. The crystal structures of complexes **3a**, **3e**, and **3f** were determined. A series of copper complexes, **3a–d**, with differently substituted dihydrooxazoles has also been synthesized.

2.2. *Solid-State Structures.* An ORTEP view [10] of copper complex **3a** is shown in Fig. 1. Complex **3a** crystallizes in the monoclinic space group $P2_1$ with two independent molecules per asymmetric unit ($Z = 4$) forming pseudodimeric complex molecules $[\text{Cu}_2\text{L}_4]$ where each Cu-atom has a distorted square pyramidal configuration. The dihydrooxazole N-atoms and phenolato O-atoms in each molecule are located in an almost square planar arrangement with a small distortion towards a tetrahedral configuration.

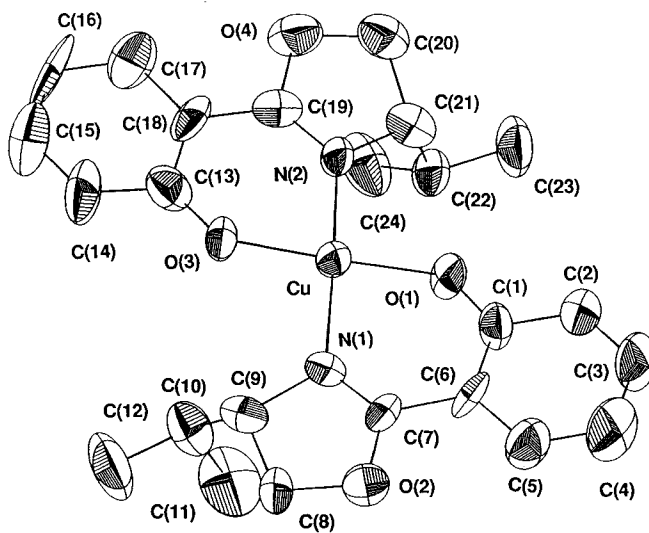


Fig. 1. *Molecular structure of 3a*. ORTEP plot, 50% probability ellipsoids with atomic numbering; H-atoms omitted for clarity.

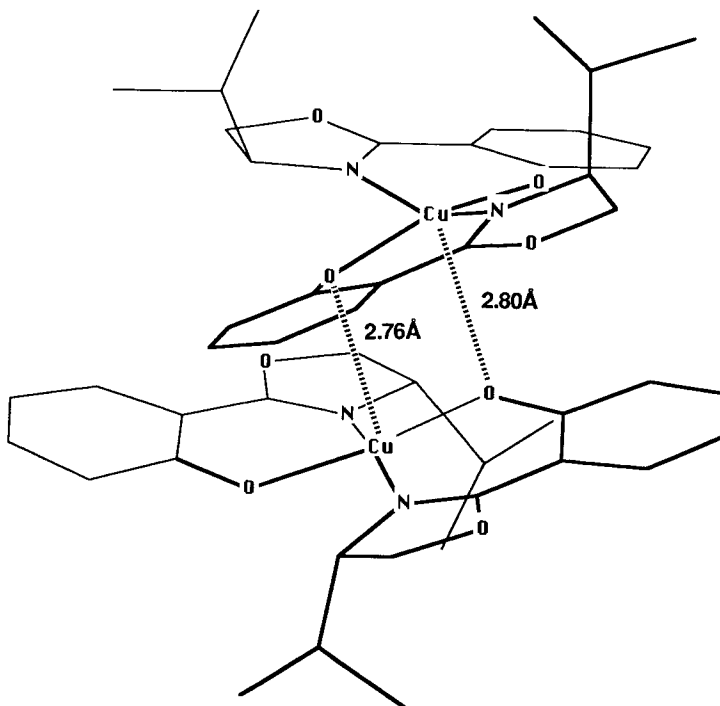


Fig. 2. *Schematic drawing of the molecular arrangement of two molecules of 3a in the crystal*. Selected atom labelling.

The deviation of the Cu-atom from the N–N–O–O plane is -0.146 Å towards the O-atoms. One of these two O-atoms is bonded to the Cu-atom of the neighboring molecule (*Fig. 2*). The Cu-atoms thereby become penta-coordinate. The intermolecular distances between the Cu- and the O-atoms of adjacent molecules are 2.76 and 2.80 Å.

Both tetrahedral and planar configurations have been reported for bis(*N*-alkylsalicylaldiminato- $\kappa O, \kappa N$)copper(II) complexes, depending on the nature of the alkyl groups [11]. For a comparison with **3**, complexes with α -branched *N*-alkyl groups should be considered. In the case of *i*-Pr or *t*-Bu groups, they were found to be pseudotetrahedral in the solid state. *E.g.*, bis(*N*-isopropylsalicylaldiminato- $\kappa O, \kappa N$)copper(II) has a tetrahedral structure with an angle between the salicylaldiminato planes of 60° , whereas the *N*-Ph-, and *N*-Me-substituted complexes are almost planar [12] [13]. Recently, *Lehn* and coworkers reported the crystal structure of a chiral bis(dihydrooxazole)copper(II) complex [14], with a dihedral angle between the two N–Cu–N planes of 52° .

In **3a**, the dihedral angles between C(5)–C(6)–C(7)–O(2) are -5.26 (molecule **A**) and -8.27° (molecule **B**), which indicates the small deviation from planarity between the benzene and 4,5-dihydrooxazole ring. The Cu–O distances of 1.91 and 1.89 Å (**A**) and 1.92 and 1.91 Å (**B**) and the Cu–N distances (1.94 and 1.95 Å for both **A** and **B**) are similar to the ones reported for bis(*N*-alkylsalicylaldiminato)copper(II) complexes. In **3a**, the angles between O(1)–Cu–N(1) and O(3)–Cu–N(2) (90.2 and 91.2° (**A**) and 92.0 and 92.6° (**B**)) are slightly smaller than comparable angles in bis(*N*-isopropylsalicylaldiminato)copper(II) (94.4 and 95.0°) [11]. Significant bond lengths and angles for **3a** are given in *Table 1*.

Table 1. Selected Interatomic Distances [Å] and Angles [°] for **3a**, with Standard Deviation in Units of the Last Significant Figure in Parentheses

	A ^{a)}	B ^{a)}		A ^{a)}	B ^{a)}
Cu–N(1)	1.941(7)	1.942(10)	O(1)–Cu–N(1)	90.2(4)	92.0(4)
Cu–N(2)	1.950(11)	1.947(9)	O(1)–Cu–O(3)	74.7(4)	165.9(4)
Cu–O(1)	1.911(7)	1.917(9)	O(1)–Cu–N(2)	89.9(4)	90.2(4)
Cu–O(3)	1.889(7)	1.908(9)	N(1)–Cu–O(3)	89.6(4)	90.8(4)
N(1)–C(7)	1.268(14)	1.325(19)	N(1)–Cu–N(2)	169.5(5)	157.2(5)
N(2)–C(19)	1.266(14)	1.303(20)	O(3)–Cu–N(2)	91.2(4)	92.6(4)

^{a)} **A** and **B** refer to two independent molecules in the asymmetric unit.

The colorless crystals of Zn^{II} complex **3e** belong to the space group *A*2 of the monoclinic system. An ORTEP plot [10] of the structure is shown in *Fig. 3*. The Zn-atom has a distorted tetrahedral coordination configuration. The coordination tetrahedron has exact (crystallographic) *C*₂ symmetry with the metal centre on one of the two twofold axis (0,*y*,0) of the unit cell. The angle between the planes containing O(1)–Zn–N(1) and O(1')–Zn–N(1'), expressed by the dihedral angle between C(1)–O(1)–Zn–N(1'), is found to be 97.65° . Least squares planes calculations give a value of 96.1° for the angle between the two planes. The planes between the benzene ring and the heterocycle are only slightly twisted. The dihedral angle between C(5)–C(6)–C(7)–O(2) is -5.37° ; that of C(5)–C(6)–C(7)–N(1) is 175.15° . The Zn–O and the Zn–N bond distances of **3e** are 1.913(2) Å and 1.976(2) Å, respectively. Whereas the former does not differ substantially

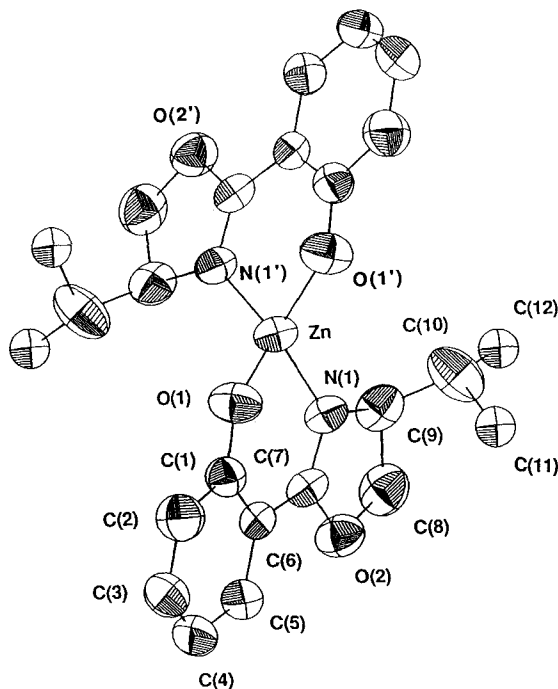


Fig. 3. Molecular structure of **3e**. ORTEP plot, 50% probability ellipsoids with atomic numbering; H-atoms omitted for clarity.

Table 2. Selected Interatomic Distances [Å] and Angles [°] for **3e** and **3f**

	3e (M = Zn)	3f (M = Ni; C) ^{a)}	3f (M = Ni; D) ^{a)}
M–N(1)	1.976(2)	1.870(3)	1.878(5)
M–O(1)	1.913(2)	1.838(4)	1.834(4)
N(1)–C(7)	1.314(3)	1.291(7)	1.282(9)
O(1)–M–N(1)	95.2(1)	92.7(2)	92.3(2)
O(1)–M–O(1')	109.6(2)	172.5(3)	173.7(3)
O(1)–M–N(1')	125.6(2)	87.5(3)	88.3(3)
N(1)–M–N(1')	109.0(2)	177.2(3)	170.9(3)

^{a)} C and D refer to two independent molecules in the asymmetric unit.

from values reported for similar *Schiff*-base complexes [15], the latter is relatively short. The angle O(1)–M–N(1) is larger in Zn^{II} complex **3e** than in Cu^{II} complex **3a** (95.2(1)° and 90.2(4) [92.0(4)]³⁾ resp.). Selected bond lengths and angles are given in Table 2.

The distorted square planar Ni^{II} complex **3f** forms stable green monoclinic crystals of space group *A*2 with two independent molecules per asymmetric unit, both having exact (crystallographic) *C*₂ symmetry with the metal centres on the two twofold axis of the side-centered lattice. The small distortion of the square plane is towards a tetrahedral configuration. The deviation of the Ni-atom from the N–N–O–O plane is –0.038 Å

³⁾ Values for the second independent molecule in brackets.

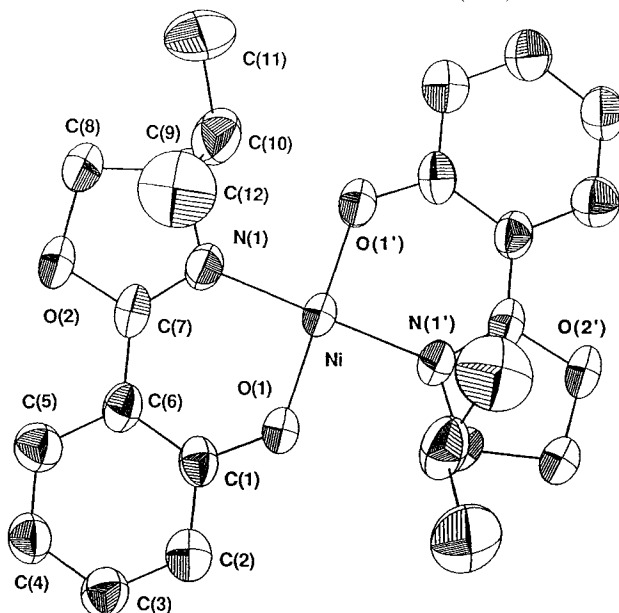


Fig.4. Molecular structure of **3f**. ORTEP plot, 50% probability ellipsoids with atomic numbering; H-atoms omitted for clarity.

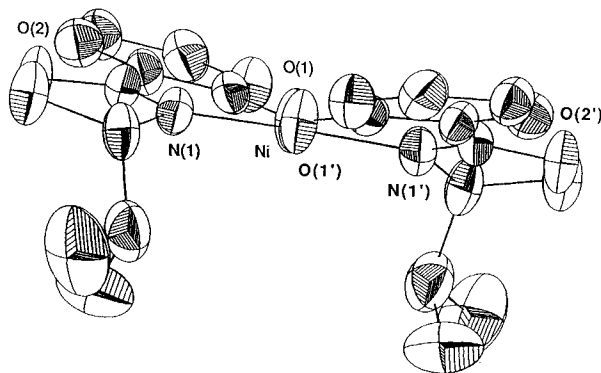


Fig.5. Side view of the molecular structure of **3f**. ORTEP plot, 50% probability ellipsoids with atomic numbering; H-atoms omitted for clarity.

towards the N atoms. No significant difference between the two complex molecules were observed. ORTEP plots [10] are shown in *Figs. 4* and *5*. In comparison, α -branched bis(*N*-isopropylsalicylaldiminato)nickel(II) is paramagnetic and isomorphous with the corresponding Cu^{II} and Zn^{II} complexes. They have a distorted tetrahedral coordination [16–18]. Bis(*N*-cyclopentylsalicylaldiminato)- and bis(*N*-cyclohexylsalicylaldiminato)-nickel(II) are diamagnetic and have a planar structure in the solid state [19]. Each of the heterocycles in **3f** is planar. The degree of distortion between the planes of the ligands is indicated by the angles between O(1)–Ni–O(1') and N(1)–Ni–N(1'), found to be

172.5(3) [173.7(3)]^{o3}) and 177.2(3) [170.9(3)]^{o3}), respectively. Ni–N (1.870(3) [1.878.(5)]Å³) and Ni–O (1.838(4) [1.834(5)]Å³) bond distances do not differ substantially from other four-coordinate complexes. Selected bond lengths and angles are shown in Table 2.

2.3. NMR Spectroscopy. Zn^{II} and Ni^{II} complexes **3e** and **3f** were studied in solution by NMR spectroscopy. Both complexes were only slightly soluble in CDCl₃ and CD₃CN.

The ¹H-NMR spectrum of **3e** in CDCl₃ shows only small chemical-shift differences compared to the spectrum of uncomplexed 4,5-dihydrooxazole **6a**. Due to the low solubility of diamagnetic Ni^{II} complex **3f** in CDCl₃, its spectrum was recorded in CD₃CN and compared with the spectrum of **6a** in the same solvent. In **3f**, all aromatic-proton signals are shifted upfield with respect to those of **6a**. The protons of the heterocycle show three distinct resonances. The chemical-shift difference $\Delta\delta$ of the Me groups in **3f** is only 0.02 ppm, as compared to 0.06 ppm in **6a**. The ¹³C-NMR spectrum of **3e** was recorded in CDCl₃. All alkyl C-signals are shifted upfield with respect to those of **6a**. The difference in chemical shift between the signals of the Me groups in **3e** increases to 2.8 ppm, as compared to 0.1 ppm for the diastereotopic Me groups in **6a**. The signals for the O-bearing aromatic C-atom and C(2) of the heterocycle are significantly shifted downfield (160.2 and 165.3 ppm for **6a**, 170.0 and 170.5 ppm for **3e**). Similar shifts are observed in Ni^{II} complex **3f**, the ¹³C-NMR spectrum of which was recorded in CD₃CN due to its low solubility in CDCl₃. As in **3e**, the chemical-shift difference for the Me signals in **3f** is relatively large (4.3 ppm). Both O-bearing C-atoms, C(2) of the aromatic ring and C(2) of the heterocycle, are found at low field (165.5 and 166.4 ppm, resp.).

3. Conclusions. – Stable metal complexes of optically active 4,5-dihydro-2-(2'-hydroxyphenyl)oxazoles are readily formed from the free ligands and metal salts in EtOH. Their coordination geometries differ from the related (salicylaldiminato)metal complexes. Their catalytic properties in asymmetric transformations are currently under active investigation.

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Experimental Part

General. The preparation of **6a** and **6d** has been described previously [6]. The yields for complexes **3a–h** are generally over 90%. M.p.: Büchi 530; uncorrected. UV: VIS($\lambda_{\max}$ (ϵ) if not stated otherwise): Hewlett-Packard 8450A UV/VIS spectrometer. IR spectra (cm⁻¹): Perkin-Elmer-781 IR spectrometer. NMR: Varian-Gemini-300 (¹H, 300 MHz; ¹³C, 75 MHz) and Varian-VXR-400 spectrometer (¹H, 400 MHz; ¹³C, 100 MHz); CDCl₃ solns. unless noted otherwise; chemical shifts in ppm rel. to internal TMS (= 0 ppm) for ¹H, rel. to CDCl₃ (= 77 ppm) for ¹³C, coupling constants *J* in Hz. MS: VG-70-250 spectrometer.

(4*S*)-4,5-Dihydro-2-(2'-hydroxyphenyl)-4-isopropylloxazole (**6a**). Synthesized as described in [6]. ¹H-NMR: 12.36 (s, 1 H); 7.63 (d, *J* = 7.8, 1 H); 7.35–7.38 (m, 1 H); 7.00 (d, *J* = 8.3, 1 H); 6.86 (t, *J* = 7.5, 1 H); 4.37–4.44 (m, 1 H); 4.08–4.15 (m, 2 H); 1.80 (sept., *J* = 6.7, 1 H); 1.01 (d, *J* = 6.7, 3 H); 0.94 (d, *J* = 6.7, 3 H). ¹H-NMR (CD₃CN): 7.65 (dd, *J* = 7.9, 1.3, 1 H); 7.40 (td, *J* = 7.5, 1.6, 1 H); 6.97 (d, *J* = 8.4, 1 H); 6.90 (t, *J* = 7.5, 1 H); 4.51–4.43 (m, 1 H); 4.20–4.11 (m, 2 H); 1.80 (sept., *J* = 6.6, 1 H); 0.99 (d, *J* = 6.6, 3 H); 0.93 (d, *J* = 6.6, 3 H).

(4*S*)-4,5-Dihydro-2-(2'-hydroxyphenyl)-4-phenylloxazole (**6b**). Synthesized as described for **6a** [6] using 2-hydroxybenzonitrile (**4a**) and (S)- α -phenylglycinol (= (2*S*)-2-amino-2-phenylethanol; **5b**). Yield 87%. B.p. 185°/2·10⁻² mbar. [α]_D²⁰ = +40.4 (*c* = 2.27, toluene), [α]_D²⁰ = +43.6, [α]_D²⁰ = +53.6, [α]_D²⁰ = +155.6, [α]_D²⁰ = +613.4. IR (neat): 3070, 3040, 2970, 2910, 1645, 1620, 1585, 1495, 1460, 1370, 1315, 1260, 1235, 1160, 1130, 1070, 1035, 950, 905, 830, 760, 700, 685, 670. ¹H-NMR: 12.14 (s, 1 H); 7.72 (dd, *J* = 7.8, 1.0, 1 H); 7.26–7.42 (m, 6 H); 7.00 (d, *J* = 8.3, 1 H); 6.90 (td, *J* = 7.6, 1.0, 1 H); 5.44 (dd, *J* = 8.3, 1.7, 1 H); 4.77 (dd, *J* = 7.5, 1.5, 1 H); 4.22 (t, *J* = 8.3, 1 H). ¹³C-NMR: 166.3 (s); 160.1 (s); 141.5 (s); 133.6 (d); 128.8 (d); 128.2 (d); 127.8 (d); 126.4 (d); 118.7 (d); 116.8 (d); 110.4 (s); 79.0 (t); 68.8 (d). EI-MS: 240 (21), 239 (100, *M*⁺), 210 (4), 209 (23), 208 (6), 181 (4), 180 (11), 148 (30), 121 (29), 120 (21), 119 (15), 104 (6), 103 (6), 93 (4), 92 (20), 91 (33), 90 (12) 89 (11), 78 (6), 77 (11), 65 (12), 64

(9), 63 (12), 51 (10), 50 (5). Anal. calc. for $C_{15}H_{13}NO_2$ (239.3): C 75.30, H 5.48, N 5.85; found: C 75.48, H 5.75, N 5.60.

(4*S*)-4-(*tert*-Butyl)-4,5-dihydro-2-(2'-hydroxyphenyl)oxazole (6c). Synthesized as described for 6a [6] using 2-hydroxybenzonitrile (4) and (2*S*)-2-amino-3,3-dimethylbutan-1-ol (5c). Yield 76%. M.p. 25°. $[\alpha]_{589}^{20} = -60.5$ ($c = 2.44$, toluene). $[\alpha]_{578}^{20} = -63.2$, $[\alpha]_{546}^{20} = -72.2$, $[\alpha]_{436}^{20} = -125.4$, $[\alpha]_{365}^{20} = -150.53$. IR (neat): 3060, 2960, 2900, 2860, 1640, 1620, 1580, 1490, 1420, 1390, 1360, 1305, 1255, 1230, 1205, 1190, 1150, 1125, 1070, 1055, 1030, 955, 910, 855, 825, 790, 750, 660. 1H -NMR: 12.39 (s, 1 H); 7.63 (dd, $J = 7.9$, 1.7, 1 H); 7.36 (dt, $J = 8.3$, 1.7, 1 H); 7.00 (d, $J = 8.4$, 1 H); 6.86 (td, $J = 8.5$, 1.0, 1 H); 4.34 (dd, $J = 10.0$, 8.7, 1 H); 4.22 (t, $J = 8.3$, 1 H); 4.11 (dd, $J = 10.0$, 7.8, 1 H); 0.94 (s, 9 H). ^{13}C -NMR: 165.1 (s); 160.0 (s); 133.2 (d); 128.0 (d); 118.5 (d); 116.7 (d); 110.6 (s); 75.0 (d); 68.0 (t); 33.8 (s); 25.8 (q). EI-MS: 220 (5), 219 (32, M^+), 163 (11), 162 (100), 161 (4), 134 (27), 121 (16), 120 (10), 107 (20), 92 (6), 91 (3), 77 (3), 65 (6), 57 (8), 41 (11). Anal. calc. for $C_{13}H_{17}NO_2$ (219.3): C 71.21, H 7.81, N 6.39; found: C 71.29, H 7.51, N 6.30.

Bis[(4*S*)-4,5-dihydro-4-isopropyl-2-(2'-oxidophenyl- κO)oxazole- κN]copper(II) (3a). A soln. of 0.091 g (0.5 mmol) of $Cu(OAc)_2$ in 10 ml of abs. EtOH was added to a soln. of 0.205 g (1 mmol) of 6a in 30 ml of abs. EtOH. After 24 h at r.t., 0.225 g (96%) of 3a were isolated as green crystals by filtration. Suitable crystals for X-ray analysis were obtained after recrystallization from EtOH. M.p. 221°. $[\alpha]_{589}^{20} = -1400$ ($c = 0.0625$, $CHCl_3$). UV/VIS (MeCN): 598 (7.11), 341 (3394), 287 (4177). IR (KBr): 2961, 1620, 1542, 1472, 1450, 1142, 1239, 1155, 1070, 855, 752. EI- and FAB-MS (NBA): 476 (1), 475 (14), 474 (48), 473 (55), 472 (100, M^+), 471 (59), 270 (10), 269 (18), 268 (32), 267 (33), 266 (19), 224 (31), 206 (24). Anal. calc. for $C_{24}H_{28}CuN_2O_4$ (472.1): C 61.06, H 5.99, N 5.94; found: C 61.09, H 6.25, N 5.83.

Bis[(4*S*)-4,5-dihydro-2-(2'-oxidophenyl- κO)-4-phenyloxazole- κN]copper(II) (3b). Prepared as described for 3a using 6b and $Cu(OAc)_2$. M.p. 238°. $[\alpha]_{589}^{20} = -1297$ ($c = 0.1$, $CHCl_3$). UV/VIS (MeCN): 584 (54.9), 344 (18430), 292 (15000). IR (KBr): 3060, 3030, 2970, 2910, 1620, 1540, 1490, 1475, 1450, 1395, 1350, 1265, 1230, 1155, 1140, 1080, 1030, 950, 935, 855, 755, 695, 665, 620. EI- and FAB-MS (NBA): 543 (16), 542 (51), 541 (61), 540 (100, M^+), 539 (56), 304 (23), 303 (41), 302 (62), 301 (75, $[CuL]^+$), 300 (30), 289 (9), 241 (3), 240 (23), 239 (16), 224 (6), 208 (6), 185 (7), 184 (4), 183 (22), 182 (10), 181 (12), 166 (3), 154 (4), 153 (24), 122 (4), 115 (7), 104 (5), 103 (6), 92 (7), 91 (24). Anal. calc. for $C_{30}H_{24}CuN_2O_4$ (540.1): C 66.72, H 4.48, N 5.19; found: C 66.52, H 4.65, N 5.14.

Bis[(4*S*)-4-(*tert*-butyl)-4,5-dihydro-2-(2'-oxidophenyl- κO)oxazole- κN]copper(II) (3c). Prepared as described for 3a using 6c and $Cu(OAc)_2$. M.p. 265°. $[\alpha]_{589}^{20} = -2160$ ($c = 0.1$, $CHCl_3$). UV/VIS (MeCN): 622 (89.1), 343 (19510), 294 (16480). IR (KBr): 3060, 2960, 2900, 2870, 1615, 1590, 1545, 1470, 1450, 1400, 1390, 1365, 1350, 1575, 1240, 1215, 1150, 1140, 1085, 1060, 1030, 955, 930, 855, 755, 725, 690, 665, 620. EI- and FAB-MS (NBA): 782 (6, $[Cu_2L_3]^+$), 780 (6), 564 (6, $[Cu_2L_2]^+$), 562 (6), 503 (12), 502 (42), 501 (48), 500 (88, M^+), 499 (52), 297 (3), 284 (24), 283 (37), 282 (74, $[CuL]^+$), 281 (69), 280 (50), 279 (6), 268 (4), 266 (4), 227 (7), 226 (46), 225 (19), 224 (100), 223 (7), 220 (10), 184 (11), 183 (17), 182 (23), 181 (23), 154 (11), 136 (8). Anal. calc. for $C_{26}H_{32}CuN_2O_4$ (500.1): C 62.44, H 6.45, N 5.60; found: C 62.63, H 6.10, N 5.43.

Bis[(4*S*,5*R*)-4,5-dihydro-4-methyl-2-(2'-oxidophenyl- κO)-5-phenyloxazole- κN]copper(II) (3d). Prepared as described for 3a using 6d and $Cu(OAc)_2$. M.p. 234°. $[\alpha]_{589}^{20} = -1294$ ($c = 0.07$, $CHCl_3$). UV/VIS (MeCN): 594 (45.4), 340 (20330), 290 (16480). IR (KBr): 3070, 3030, 2980, 2930, 1620, 1540, 1500, 1470, 1450, 1395, 1350, 1270, 1235, 1155, 1140, 1125, 1095, 1070, 1030, 1005, 1000, 960, 920, 855, 805, 755, 700, 670, 665, 640. EI- and FAB-MS (NBA): 571 (18), 570 (51), 569 (63), 568 (100, M^+), 567 (63), 318 (10), 317 (17), 316 (44, $[CuL]^+$), 315 (35), 314 (27), 254 (21), 253 (13), 224 (3), 198 (6), 197 (7), 196 (20), 195 (7), 194 (8), 185 (10), 183 (25), 182 (7), 181 (20), 165 (3), 153 (6), 133 (3), 132 (9), 121 (12), 117 (11), 115 (4), 91 (9), 53 (21). Anal. calc. for $C_{32}H_{28}CuN_2O_4$ (568.1): C 67.65, H 4.97, N 4.93; found: C 66.96, H 4.95, N 4.94.

Bis[(4*S*)-4,5-dihydro-4-isopropyl-2-(2'-oxidophenyl- κO)oxazole- κN]zinc(II) (3e). Prepared as described for 3a using 6a and $Zn(OAc)_2$. M.p. 288°. $[\alpha]_{589}^{20} = +245$ ($c = 0.49$, $CHCl_3$). UV (MeCN): 378 (26.2), 345 (7236). IR (KBr): 2960, 2920, 1615, 1465, 1444, 1391, 1340, 1255, 1235, 1158, 1070. 1H -NMR: 7.67 (dd, $J = 8.1$, 1.9, 1 H); 7.30 (ddd, $J = 8.7$, 6.9, 1.9, 1 H); 6.87 (d, $J = 8.5$, 1 H); 6.53 (ddd, $J = 8.1$, 6.9, 1.2, 1 H); 4.39–4.44 (m, 1 H); 4.22–4.29 (m, 2 H); 1.91–1.95 (m, 1 H); 0.87 (d, $J = 7$, 3 H); 0.85 (d, $J = 6.9$, 3 H). EI- and FAB-MS (NBA): 746 (1, $[L_3Zn]^+$), 745 (1), 744 (5), 742 (5), 740 (4), 479 (1), 478 (9), 477 (39), 476 (43), 475 (64), 474 (51), 473 (100, M^+), 472 (45), 471 (8), 270 (23), 268 (39), 206 (40), 205 (30). Anal. calc. for $C_{24}H_{28}N_2O_4Zn$ (473.9): C 60.82, H 5.97, N 5.91; found: C 61.05, H 6.11, N 5.64.

Bis[(4*S*)-4,5-dihydro-4-isopropyl-2-(2'-oxidophenyl- κO)oxazole- κN]nickel(II) (3f). Prepared as described for 3a using 6a and $Ni(OAc)_2$. M.p. 192°. $[\alpha]_{589}^{20} = +2280$ ($c = 0.05$, $CHCl_3$). UV/VIS (MeCN): 612 (60.1), 498 (85.3), 377 (13340), 364 (13810), 304 (20250). IR (KBr): 3060, 2960, 2870, 1630, 1545, 1485, 1470, 1450, 1405, 1350, 1270, 1245. 1H -NMR (CD_3CN): 7.41 (d, $J = 8.0$, 2 H); 7.14 (t, $J = 7.5$, 2 H); 6.54 (d, $J = 8.7$, 2 H); 6.43 (t, $J = 7.4$, 2 H); 4.46 (dd, $J = 9.1$, 3.0, 2 H); 4.30 (t, $J = 9.1$, 2 H); 4.12 (d, $J = 8.6$, 2 H); 2.44 (m, 2 H); 1.01 (t, 6.4, 12 H).

^{13}C -NMR (CD_3CN): 166.4 (*s*); 165.5 (*s*); 134.4 (*s*); 128.7 (*d*); 123.8 (*d*); 115.5 (*d*); 110.0 (*s*); 69.7 (*d*); 65.6 (*r*); 32.3 (*d*); 19.2 (*q*); 14.9 (*q*). EI- and FAB-MS (NBA): 730 (21), 729 (11), 728 (25, $[\text{L}_3\text{Ni}]^+$), 524 (6), 470 (17), 469 (43), 467 (100, M^+), 466 (96), 465 (12), 423 (6), 264 (17), 263 (27), 262 (39, $[\text{LNi}]^+$), 261 (20), 232 (5), 219 (9), 218 (9), 206 (22), 178 (20), 177 (14), 176 (43). Anal. calc. for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{NiO}_4$ (467.2): C 61.70, H 6.04, N 6.00; found: C 61.71, H 6.14, N 6.08.

Bis[(4S)-4,5-dihydro-4-isopropyl-2-(2'-oxidophenyl- κO)oxazole- κN]cobalt(II) (3g). Prepared as described for **3a** using **6a** and $\text{Co}(\text{OAc})_2$. M.p. 282° . $[\alpha]_{589}^{20} = +460$ ($c = 0.055$, CHCl_3). UV/VIS (MeCN): 530 (11.9), 474 ($\log \epsilon$ 8.63), 343 (18700), 309 (13310), 277 (19500). IR (KBr): 3070, 2970, 2930, 2880, 1615, 1590, 1540, 1485, 1470, 1445, 1400, 1390, 1345, 1260, 1240, 1160, 1070. EI- and FAB-MS (NBA): 731 (4), 730 (13, $[\text{L}_3\text{Co}]^+$), 469 (24), 468 (100), 467 (64, M^+), 466 (6), 460 (5), 424 (5), 383 (3), 264 (5), 263 (31, $[\text{LCo}]^+$), 261 (4), 219 (11), 206 (27), 205 (18), 177 (46), 162 (6). Anal. calc. for $\text{C}_{24}\text{H}_{28}\text{CoN}_2\text{O}_4$ (467.4): C 61.67, H 6.04, N 5.99; found: C 61.49, H 5.85, N 5.95.

Chlorobis[(4S)-4,5-dihydro-4-isopropyl-2-(2'-oxidophenyl- κO)oxazole- κN]iron(III) (3h). Prepared as described for **3a** using **6a** and FeCl_3 . M.p. 238° . $[\alpha]_{589}^{20} = -491$ ($c = 0.003$, CHCl_3). UV/VIS (MeCN): 464 (3571), 368 (3907), 295 (11720). IR (KBr): 3030, 2970, 2940, 2880, 1615, 1590, 1550, 1485, 1470, 1450, 1400, 1385, 1330, 1265, 1240, 1160, 1075. EI- and FAB-MS (NBA): 669 (2), 500 (8, M^+), 466 (8), 465 (41), 464 (100, $[\text{FeL}_2]^+$), 463 (13), 462 (8), 378 (5), 295 (3), 292 (3), 260 (10, $[\text{FeL}]^+$), 258 (3), 252 (3), 216 (8), 207 (13), 206 (93), 205 (11), 204 (6), 174 (27), 162 (7), 121 (4). Anal. calc. for $\text{C}_{24}\text{H}_{28}\text{ClFeN}_2\text{O}_4$ (499.8): C 57.68, H 5.65, N 5.61; found: C 57.40, H 5.67, N 5.51.

X-Ray Structure Analysis of 3a, 3e, and 3f. Crystal data and acquisition parameters are given in Table 3. Suitable crystals for X-ray analysis were obtained by slow evaporation of the solvent at r.t. Data collection was carried out on an *Enraf-Nonius-CAD-4* diffractometer using the $\omega/2\theta$ scan mode. The structures were solved by *Patterson* techniques using the program SHELXS-86 [20]. No corrections for absorption were applied. Anisotropic full-matrix least-squares refinements were carried out for all non-H-atoms. H-Atoms were calculated with a C–H distance of 1.08 Å and refined isotropically using fixed thermal U values of 0.05. Final parameters and a list of bond

Table 3. Crystal Data and Data Collection Parameters for **3a**, **3e**, and **3f**

	3a	3e	3f
Molecular formula	$\text{C}_{24}\text{H}_{28}\text{CuN}_2\text{O}_4$	$\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_4\text{Zn}$	$\text{C}_{24}\text{H}_{28}\text{N}_2\text{NiO}_4$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$A2$	$A2$
a [Å]	11.725(2)	12.034(3)	11.389(3)
b [Å]	17.404(1)	5.640(3)	10.068(3)
c [Å]	12.062(3)	19.359(5)	20.605(5)
α [°]	90.0	90.0	90.0
β [°]	109.03(2)	117.89(3)	92.83(3)
γ [°]	90.0	90.0	90.0
V [Å ³]	2327.0(3)	1161.2(2)	2359.7(2)
Z	4	2	4
θ_{max}	28	28	28
Cryst. dims. [mm]	$0.1 \times 0.1 \times 0.3$	$0.3 \times 0.2 \times 0.2$	$0.3 \times 0.2 \times 0.2$
Temperature [K]	293	293	293
Radiation	MoK_α	MoK_α	MoK_α
λ [Å]	0.71069	0.71069	0.71069
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Coll. refl.	$\pm h, +k, +l$	$\pm h, +k, +l$	$\pm h, +k, +l$
μ [cm ⁻¹]	9.69	11.12	8.54
$F(000)$	988	496	984
No. of independent refl.	5799	2513	2994
No. of refl. in refinement	3357	1165	2506
No. of variables	580	148	292
Observations/variables	5.79	7.87	8.58
Final R_w factor	0.078 ^a	0.074 ^a	0.060
Weighting scheme	$1.52/(\sigma(F^2) + 1.35 \cdot 10^{-3} F^2)$	$3.58/(\sigma(F^2) + 1.24 \cdot 10^{-2} F^2)$	$1.0/(\sigma(F^2) + 4.96 \cdot 10^{-3} F^2)$

^a) The bad R values are a consequence of the crystal qualities.

lengths and angles are deposited at the *Cambridge Crystallographic Data Centre*, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

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