

Book Chapter

One-Step Templated Synthesis of Chiral Organometallic Salicyloxazoline Complexes

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Abstract

Background: The general approach for the synthesis of metal complexes begins with the preparation of ligands, followed by reacting the ligands with metal salts to afford organometallic complexes. Our research group first reported a one-pot multicomponent synthesis of chiral oxazolinyl-zinc complexes, and our two-step procedure can be extended in the presence of a large amount of ZnCl_2 (0.4-2.6 equiv.), with the yields of some products reaching 90%. The chiral salicyloxazoline metal complexes can be produced using 1.0 equiv. of copper, cobalt, nickel, manganese, palladium and platinum salts as the third component.

Results: A one-step method used 1.0 equivalent of a metal salt, such as $\text{M}(\text{OAc})_2 \cdot n\text{H}_2\text{O}$ or $\text{MCl}_2 \cdot n\text{H}_2\text{O}$ (M: Cu, Ni, Co, Pd or Pt, $n = 1, 2$ or 4), as a reagent to generate chiral salicyloxazoline

complexes **1–8** in the reaction of 2-cyanophenol with different D- and L-amino alcohols.

Conclusion: Complexes **1–8** were obtained using a one-pot method with a sequential strategy. The reaction outcome was demonstrated for three-component reactions between metal salts, amino alcohols and 2-hydroxybenzonitrile to afford organometallic complexes in good yields (65%–95%).

Keywords

One-Step Method; Salicyloxazoline Complexes; Metal Salts; 2-Cyanophenol; D- and L-Amino Alcohols

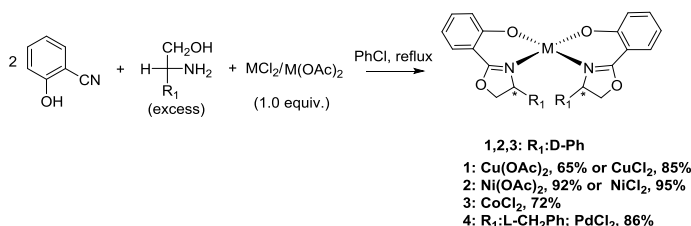
Introduction

Chiral oxazolinyl organometallic complexes are very important catalysts in organic chemistry [1]. Several organometallic complexes containing 2-(2'-hydroxyphenyl)oxazolines are reported in the literature, [2-9] and these complexes exhibit good catalytic effects in asymmetric Baeyer-Villiger reactions, [3] cyclopropanations, [8-9] and reductions of perchlorate with sulfides under mild conditions [10]. The general approach for the synthesis of metal complexes begins with ligand synthesis, followed by reacting the ligands with metal salts to afford organometallic complexes. [11] Our research group first reported a one-pot multicomponent synthesis of chiral oxazolinyl-zinc complexes, [12] and our two-step procedure can be extended in the presence of a large amount of ZnCl_2 (0.4-2.6 equiv.), with the yields of some products reaching 90%. Herein, we report that chiral salicyloxazoline metal complexes can be produced using 1.0 equiv. of copper, cobalt, nickel, manganese, palladium and platinum salts as the third component. The structures were confirmed using X-ray crystallography.

Results and Discussion

Chiral bis(oxazoline) copper complex **1**, nickel complex **2**, cobalt complex **3** and palladium complex **4** were generated as crystals with the chemical formula ML_2 ($\text{L} = 2\text{-(4-R}_1\text{-4,5-dihydrooxazol-2-yl)phenol}$, R_1 : D-Ph, M: Cu, Ni, Co; R_1 : L- CH_2Ph ; M: Pd). The syntheses of these complexes are described

below. A mixture of 2-hydroxybenzonitrile and the appropriate D/L-amino alcohol in 50 mL of chlorobenzene was refluxed for 72 h with 1.0 equiv. of copper chloride dihydrate or 1.0 equiv. of copper(II) acetate monohydrate, 1.0 equiv. of nickel chloride hexahydrate or 1.0 equiv. of nickel acetate tetrahydrate, 1.0 equiv. of cobalt chloride hexahydrate, or 1.0 equiv. of palladium chloride. The reaction mixture was purified by the removal of chlorobenzene followed by extraction and recrystallization or by extraction and column chromatography separation with petroleum ether and dichloromethane. Natural evaporation of the recrystallization or chromatographic solvent provided single crystals of chiral bisoxazolinyl metal complexes **1–4** (**Scheme 1** and **Figs. 1–4** in the supporting materials).

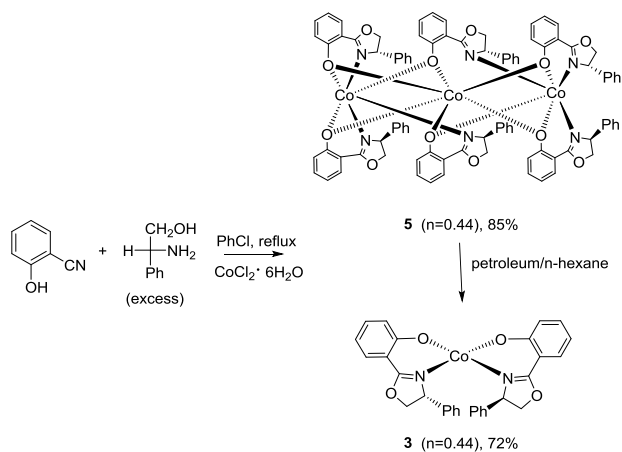


Scheme 1: Templated synthesis of complexes 1-4.

The chiral oxazoline cobalt complexes **5** and **6** were prepared by refluxing a mixture of 2-cyanophenol and D-phenylglycinol in chlorobenzene for 72 h with 1.0 equiv. of cobalt chloride hexahydrate or 1.0 equiv. of cobalt acetate tetrahydrate, respectively (**Schemes 2** and **3**, respectively). Crystals of complex **5** were obtained by slow evaporation from a 1:1 mixture of ethanol and chloroform (**Figure 1**: right). However, the crystals of complex **6** were obtained after column chromatography with a 4:1 solution of petroleum ether and dichloromethane, followed by evaporation of the volatile components (**Figure 2**: left).

Notably, the products of complexes **3** and **5** were obtained using CoCl_2 as a reagent with different solvents in the workup procedure. When a nonpolar solvent, such as petroleum ether or n-hexane, was used in the recrystallization medium, the crystal structure of complex **3** was obtained. However, if the

recrystallization was carried out with a mixture of two polar solvents, such as ethanol and chloroform, complex **5** crystals were obtained (**Scheme 2**). Both crystal structures are shown in **Figure 1** (left: complex **3**, right: complex **5**).



Scheme 2: Effect of different solvents on the formation of complexes **3** and **5**.

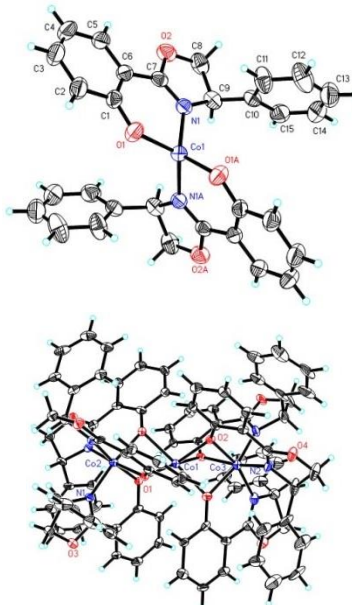
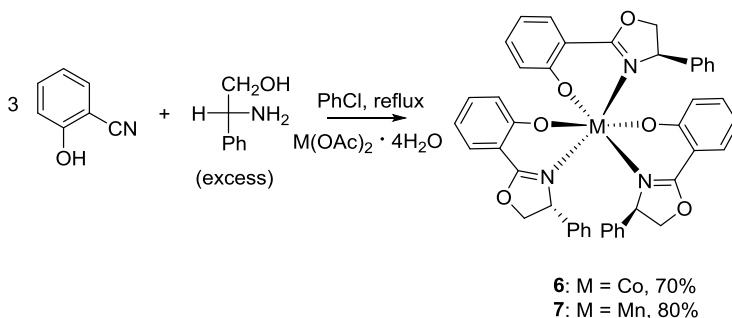


Figure 1: ORTEP view of complexes **3** (left) and **5** (right).

Similarly, in the synthesis of chiral oxazoline manganese complex **7** by the title method, 2-hydroxybenzonitrile and D-phenylglycinol were dissolved in chlorobenzene and refluxed in the presence of 1.0 equiv. of manganese acetate tetrahydrate for 60 h (**Scheme 3**). Crystals of complex **7** (**Figure 2**: right) were obtained by slow evaporation from a mixture of absolute ethanol and chloroform.



Scheme 3: One-pot synthesis of tri(oxazoline) metal complexes **6** and **7**.

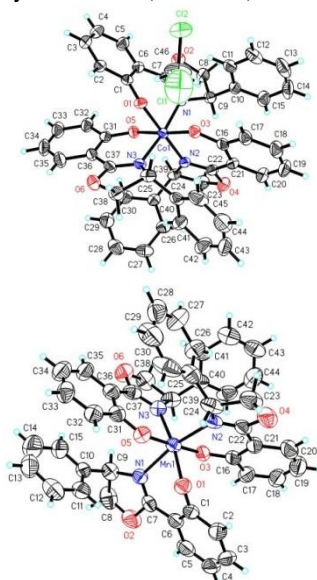
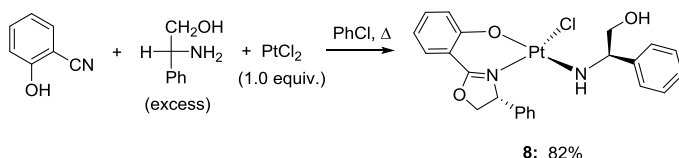


Figure 2: ORTEP view of complexes **6** (left) and **7** (right).

Interestingly, when 1.0 equiv. of PtCl_2 was employed in the reaction of 2-hydroxybenzonitrile with D-phenylglycinol in

chlorobenzene, the crystal structure of the resulting Pt complex was different from those obtained with the previously mentioned metal salts. Complex **8**, which contains one unit of (*R*)-2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenol and one unit of D-phenylglycinol, was obtained after column chromatography with petroleum ether and dichloromethane (4:1) followed by crystallization via slow evaporation (Scheme 4, Figure 3).



Scheme 4: One-pot synthesis of platinum oxazoline complex **8**.

The proposed mechanism indicates that excess metal salts can greatly activate the reactants in the reaction of 2-hydroxybenzonitrile with D-phenylglycinol in chlorobenzene to directly afford the corresponding organometallic complexes, followed by the formation of the ligand intermediates via a one-step procedure.

Table 1: Summary of the metal salts used, the products obtained, and the percentage yields in the reactions.

Table 1: One-pot synthesis of complexes **1–8** from the nitriles.

Metal salt	Amount of metal salt (mol %)	Products	Yield (%)
Cu(OAc) ₂ • H ₂ O	55.7	1	65
CuCl ₂ • 2H ₂ O	53.2	1	85
Ni(OAc) ₂ • 4H ₂ O	51.0	2	92
NiCl ₂ • 6H ₂ O	53.0	2	95
CoCl ₂ • 6H ₂ O	44.3	3, 5	72, 85
PdCl ₂	49.8	4	86
Co(OAc) ₂ • 4H ₂ O	42.3	6	70
Mn(OAc) ₂ • 4H ₂ O	52.6	7	80
PtCl ₂	33.7	8	82

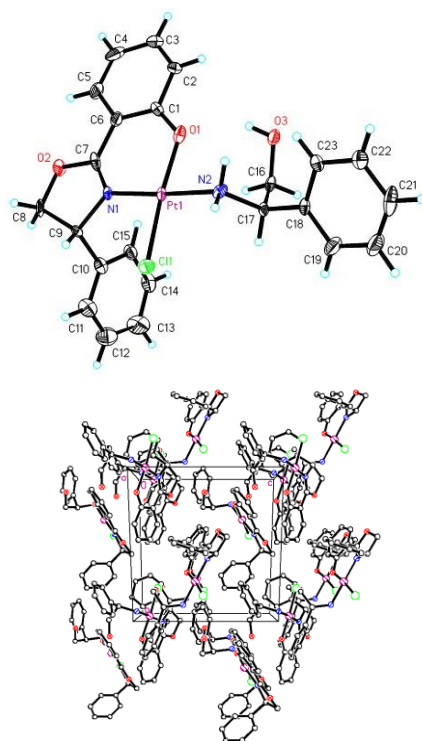


Figure 3: ORTEP view of complex **8** and packing of the molecule in a unit cell.

In complexes **1–4**, the two oxazoline ligands arrange their donor atoms in a trans-planar configuration, and the structure features a four-coordinate metal center in a slightly distorted arrangement. The metal center is coordinated with the nitrogen atoms of the oxazolines and oxygen atom donated from the phenolate. The average length of the metal-N bond in complexes **1–4** are: Pd-N 2.003(7) Å > Co-N 1.983(5) Å > Cu-N 1.952(1) Å > Ni-N 1.893(3) Å, which are the same order as the average metal-O bond lengths for complexes **1–4** (e.g., Pd-O 1.986(6) Å > Co-O 1.925 (4) Å > Cu-O 1.924(9) Å > Ni-O 1.825(8) Å).

The crystal packing structure of complex **5** exhibits a sandwich-like structure and consists of three complex **3** (cobalt (II) chelates) connected by three Co(II) atoms, which generate 2D supramolecular networks. The molecular structure is depicted in

Figure 1 (right). The three cobalt (II) atoms in complex **5** form a linear trimer with a Co2-Co1-Co3 bond angle of 180°. In addition, the nonbonded Co··Co distances range from 2.823(3) to 2.832(3) Å, and the coordination sphere is different. The phenyl groups exhibit an all-cis arrangement. The central cobalt ion is at a highly symmetric center, and this cobalt atom is coordinated to six hydroxyl oxygen atoms from the phenolates. The Co(1)-O bond lengths vary in the 2.059(5)–2.112(5) Å range, and the three equal bond lengths [2.059(5) Å] of Co(1)-O(2), Co(1)-O(2)#1 and Co(1)-O(2)#2 are shorter than the three equal bond lengths [2.112(5) Å] of Co(1)-O(1), Co(1)-O(1)#1 and Co(1)-O(1)#2. The two terminal cobalt (II) chelates Co(2) and Co(3) are octahedrally coordinated with two phenoxy ligands as well as one adjacent nitrogen atom and one pendant oxygen atom from separate Co(1) phenoxy ligands. The three equal distances for Co(2)-N are 1.923(5) Å and Co(3)-N are 2.098(6) Å, which are slightly longer than the corresponding Co-O bond lengths of 1.912(5) and 2.085(5) Å.

The molecular structures of complexes **6** and **7** were determined by single-crystal X-ray diffraction analysis. It is important to note that the entire molecule is in the independent part, occupying the general position of the P21/c symmetry group. In the structures of **6** and **7**, the O and N atoms from the three phenoxy ligands are coordinated to Co³⁺ or Mn³⁺ with distorted square planar geometries, and the three ligands lie in the adjacent positions. All coordinated ligands act as chelate-forming agents and close the rings using the metal cation. Due to the Jahn-Teller effect, the axial and equatorial Co-N bonds (1.956(2), 1.937(2) and 1.951(2) Å) in complex **6** are shorter than those of the Mn-N bonds in complex **7** (2.281(5), 2.024(5) and 2.024(5) Å). However, the Co-O bond lengths (1.895(18), 1.893(19) and 1.881(18) Å) are not the same order compared to the Mn-O bond lengths (1.930(4), 1.848(4), 1.870(4) Å).

The coordination angles for **6** and **7** vary between 84.2° and 179.9°. A slight compression of the M(phenox)₃ units perpendicular to the Co: O(1)-N(3)-O(3), Mn: O(1)-O(3)-O(3) and the trigonal face was observed, leading to O(1)-Mn-N(1) angles of 81° and O(1)-Co(1)-N(3) and O(5)-Co(1)-N(1) angles

of 84°. The crystal structure of complex **8** (**Figure 3**, left) showed the presence of discrete mononuclear molecules, which were separated by van der Waals distances. The complex exhibits a nearly square-planar geometry with two equatorial nitrogen atoms, one from the oxazoline ring (Pt-N(1): 2.036 (14) Å) and one from the amino alcohol in the trans position (Pt-N(2): 1.999 (12) Å). The coordinated amine, hydroxyl group and uncoordinated hydroxyl group are involved in enriched supramolecular networks through hydrogen bonds (i.e., O(3)-H(3)···O(1) 2.813(18) Å and N(2)-H(2B)···O(3)#1 3.032(19)) (**Figure 3**, right).

The contributions of the resonance structures shown in Figs. **1–8** result in the C-N and C-O bonds of the oxazolyl ring exhibiting partial double bond character. A structure search of oxazolylphenolate complexes in the Cambridge Crystallographic Database resulted in an average C-N value of 1.291 Å (range 1.205–1.349 Å) and an average C-O value of 1.347 Å (range 1.304–1.424 Å). All C-N and C-O distances in the reported complexes fall within these expected ranges, and no systematic relationship was observed between the distance and the ligand torsion angle.

Some selected bond lengths and angles for Figs. **1–8** are presented in **Table 2** (supporting materials), and some hydrogen bond lengths and angles for complex **8** are also shown in **Table 3** (supporting materials).

The X-ray crystal structures of the complexes were determined and are reported in the supporting information. In all cases, a distorted tetrahedral geometry is found at the metal(II) ion, and the C=N double bond character of the oxazolindinyl ligand is largely retained in the metal complexes.

Experimental

General

Unless otherwise stated, 2-hydroxybenzonitrile, D-phenylglycinol, L-phenylalaninol, Cu(OAc)₂·H₂O, CuCl₂·2H₂O, Ni(OAc)₂·H₂O, NiCl₂·6H₂O, CoCl₂·6H₂O, Co(OAc)₂·4H₂O,

Mn(OAc)₂·4H₂O, and PdCl₂, PtCl₂ were purchased from Acros, Aldrich, or Fluka (USA). Flash column chromatography was performed using Merck silica gel (60, particle size 0.02-0.03 mm). The ¹H and ¹³C NMR spectra were recorded using Bruker AM-500 or AM-600 spectrometers. The chemical shifts are reported in ppm (δ) with the solvent referenced to tetramethylsilane (TMS) as the internal standard (residual CHCl₃, δ_H 7.26 ppm; CDCl₃, δ_C 77 ppm). The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, and m = multiplet. The infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer, and the peaks are reported in cm⁻¹. Elemental analyses were obtained on an Elemental Analyzer AE-3000. The high-resolution mass spectra (HRMS) were obtained on a Micro GCT-MS equipped with an EI ion source. Optical rotations were measured on a WZZ-1 automatic polarimeter with a 2 cm cell and recorded at the sodium D-line.

Bis(ligand) copper (II) chelate (CuL₂)

1. A dry 100 mL Schlenk flask was purged with N₂ and charged with Cu(OAc)₂·H₂O (2.2198 g, 11.14 mmol) or CuCl₂·2H₂O (2.1199 g, 10.64 mmol), 2-cyanophenol (2.3808 g, 19.99 mmol) and D-phenylglycinol (3.8002–4.2003 g). Then, 40 mL of chlorobenzene was added, and the reaction mixture was refluxed for 72 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was dissolved in 15 mL of H₂O followed by extraction with CH₂Cl₂ (3 x 20 mL). The combined organic extracts were evaporated to yield a crude green oil, which was purified by column chromatography (petroleum ether/CH₂Cl₂, 4/1) to afford the title compound as colorless crystals 1.9553 g in 65% yield or 2.4422 g in 85% yield; m.p.: >240 °C, [α]_D²⁵ = +235.7° (c = 0.0488, CH₃OH). ν_{max} (cm⁻¹): 3439, 3025, 2967, 2902, 1617, 1583, 1541, 1475, 1447, 1394, 1349, 1266, 1155, 1077, 1030, 949, 935, 855, 755, 695, 666, 574, 533, 414. Elemental analysis for C₃₀H₂₄N₂O₄Cu requires C: 66.72%, H: 4.44, N: 5.18%; found: C: 66.22%, H: 4.39%, N: 5.26%.

Bis(ligand) nickel (II) chelate (NiL₁₂)

2. Bis(ligand) nickel (II) chelate (NiL₁₂) was prepared using the procedure described for compound **1** by refluxing a mixture of 2-cyanophenol (2.3001 g, 19.33 mmol), Ni(OAc)₂·4H₂O (2.4528 g, 9.86 mmol) or NiCl₂·6H₂O (2.4374 g, 10.25 mmol) and D-phenylglycinol (4.2318 g) in 40 mL of dry chlorobenzene for 60 h. The product was obtained as dark brown crystals (2.5112 g in 92% yield or 2.6949 g) in 95% yield after column chromatography (petroleum ether/CH₂Cl₂, 4/1). m.p.: 196–198 °C, $[\alpha]_D^{25} = +119.57^\circ$ (c = 0.0488, CH₃OH), m.p.: 196–198 °C, $[\alpha]_D^{25} = +119.57^\circ$ (c = 0.0488, CH₃OH), ¹H NMR (600 MHz, CDCl₃ and DMSO, 27 °C): 7.85–7.86 (m, 2H), 7.22–7.49 (m, 12H), 6.46(d, J=7.3 Hz, 2H), 6.30 (t, J=6.4 Hz, 2H), 5.70–5.98 (m, 2H), 4.54–4.62 (m, 2H), 4.32–4.41 (m, 2H); δ_c (150 MHz, CDCl₃): 164.5, 164.4, 142.3, 133.5, 127.3, 126.0, 125.7, 124.3, 113.1, 107.8, 107.7(x2), 72.6, 72.5, 67.0, 65.1, 65.0. ν_{max} (cm⁻¹): 3453, 3024, 2906, 1617, 1541, 1475, 1447, 1394, 1349, 1265, 1231, 1154, 1077, 1029, 949, 931, 85.5, 755, 695, 574, 533, 415. Elemental analysis for C₃₀H₂₄N₂O₄Ni requires C: 67.32%, H: 4.52%, N: 5.23%; found: C: 67.22%, H: 4.39%, N: 5.26%.

Bis(ligand) cobalt (II) chelate (CoL₁₂)

3. Bis(ligand) cobalt (II) chelate (CoL₁₂) was prepared using the procedure described for compound **1** by refluxing a mixture of CoCl₂·6H₂O (1.5671 g, 6.59 mmol), 2-cyanophenol (1.7699 g, 14.86 mmol) and D-phenylglycinol (3.6798 g) in 40 mL of dry chlorobenzene for 60 h. The product was obtained as red-brown crystals (1.7079 g) in 72% yield after evaporation from a mixture of petroleum or *n*-hexane, absolute ethanol or dichloromethane (1:1); m.p.: 146–147 °C, $[\alpha]_D^{25} = -149.2^\circ$ (0.054, CH₃OH), ¹H NMR (600 MHz, CDCl₃ and DMSO, 27 °C): 7.68 (d, J= 6.7 Hz, 2H), 7.29–7.48 (m, 14H), 6.95–7.00 (m, 2H), 5.50–5.53 (m, 2H), 4.87 (t, J=8.4 Hz, 2H), 4.23–4.26 (m, 2H); δ_c: 166.3, 160.0, 141.5, 133.6, 128.8, 128.2, 127.9, 127.8, 126.5, 118.7, 116.8, 110.4, 74.0, 68.8. ν_{max} (cm⁻¹): 3411, 3127, 2928, 1614, 1617, 1591, 1536, 1493, 1475, 1456, 1439, 1388, 1255, 1236, 1157,

1074, 1056, 954, 932, 913, 851, 753, 699, 660, 615, 567, 530, 415. Elemental analysis for $C_{30}H_{24}N_2O_4Co$ requires C: 67.54%, H: 4.53%, N: 6.34%; found: C: 67.87%, H: 4.86%, N: 6.33%.

Bis(ligand) palladium (II) chelate (PdL₂)

4. Bis(ligand) palladium (II) chelate (PdL₂) was prepared using the procedure described for compound **1** by refluxing a mixture of PdCl₂ (0.8836 g, 4.98 mmol), 2-cyanophenol (1.1927 g, 10.01 mmol) and L-phenylalaninol (2.3579 g) in 40 mL of dry chlorobenzene for 60 h. The product was obtained as dark brown crystals (2.6166 g) in 86% yield after column chromatography (petroleum ether/CH₂Cl₂, 4/1); m.p.: 146–148 °C, $[\alpha]_D^{25} = -24.19^\circ$ (c 0.0248, CH₃OH): ¹H NMR (300 MHz, CDCl₃, 27 °C), δ (ppm) = 7.44–7.47 (m, 5H), 7.24–7.31 (m, 10H), 6.85 (d, J=0.8 Hz, 2H), 6.54 (t, J=0.6 Hz, 1H), 4.74–4.78 (m, 2H), 4.49–4.54 (m, 3H), 3.35–3.41 (m, 2H), 2.83–2.91 (m, 3H); ¹³C NMR: 168.0, 162.3, 137.7, 134.7, 130.1, 129.9, 129.8, 129.2, 127.3, 121.7, 115.4, 109.5, 72.3, 62.3, 60.2, 54.5, 35.5. ν_{max} (cm⁻¹): 3025, 1611, 1540, 1496, 1467, 1438, 1396, 1343, 1257, 1253, 1234, 1154, 1140, 1084, 1065, 1029, 973, 938, 856, 750, 725, 698, 683, 671, 620, 597, 577. Elemental analysis for C₃₂H₂₈N₂O₄Cl₂Pd requires C: 56.36%, H: 4.14%, N: 4.11%; found: C: 56.48%, H: 4.22%, N: 4.38%.

Bis(ligand) cobalt (II) chelate trimer (CoL₁₂)₃

5. Bis(ligand) cobalt (II) chelate trimer (CoL₁₂)₃ was prepared using the procedure described for compound **1** by refluxing a mixture of CoCl₂·6H₂O (1.5671 g, 6.29 mmol), 2-cyanophenol (1.7699 g, 14.86 mmol) and D-phenylglycinol (3.8256 g) in 40 mL of dry chlorobenzene for 60 h. The product was obtained as red-brown crystals 6.0489 g in 85% yield after evaporation from a mixture of ethanol and chloroform (1:1); m.p.: 193–194 °C. ¹H NMR (600 MHz, CDCl₃ and DMSO, 27 °C), δ (ppm) = 8.28 (d, J=3.4 Hz, 1H), 7.71 (d, J=7.2 Hz, 2H), 7.32–7.49 (m, 12H), 6.97–7.02 (m, 3H), 5.55 (d, J=7.6 Hz, 2H), 4.91 (t, J=9.0 Hz, 1H), 4.13–4.39 (m, 3H), δ_C (150 MHz, CDCl₃, 27 °C): 163.5, 157.3, 139.6, 131.9, 126.8, 126.7, 126.6, 126.0, 125.7, 125.6,

124.5, 117.0, 114.5, 108.0, 72.0, 65.9, 54.1, 46.7. ν_{\max} (cm^{-1}): 3061, 3030, 2965, 1613, 1550, 1478, 1441, 1397, 1339, 1232, 1157, 1073, 1057, 999, 952, 939, 856, 749, 698, 581. Elemental analysis for $\text{C}_{90}\text{H}_{72}\text{Co}_3\text{N}_6\text{O}_{12}$ requires C: 67.30%, H: 4.48%, N: 5.23%; found: C: 67.23%, H: 4.70%, N: 4.90%.

Tri(ligand) cobalt chelate (CoL1_3)

6. Tri(ligand) cobalt chelate (CoL1_3) was prepared using the procedure described for compound **1** by refluxing a mixture of 1.5671 g of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (6.29 mmol), 2-cyanophenol (1.7699 g, 14.86 mmol) and D-phenylglycinol (3.6798 g) in 40 mL of dry chlorobenzene for 60 h. The product was obtained in 70% yield (2.5424 g) as dark brown crystals after column chromatography (petroleum ether/ CH_2Cl_2 , 4/1). Yield %: 70%; m.p.: 174–176 °C, $[\alpha]_D^{25} = -1014.1^\circ$ (0.0212, CH_3OH), δ_{H} (600 MHz, CDCl_3 , 27 °C) 7.50–7.52 (m, 1H), 7.23–7.24 (m, 1H), 7.02–7.07 (m, 2H), 6.87–6.97 (m, 9H), 6.74–6.80 (m, 7H), 6.56 (d, $J=8.56$ Hz, 1H), 6.45–6.49 (m, 3H), 6.41 (d, $J=8.5$ Hz, 1H), 6.24–6.27 (m, 2H), 5.45–5.48 (m, 1H), 5.29–5.32 (m, 1H), 4.91–4.92 (m, 2H), 4.79–4.82 (m, 2H), 4.33–4.36 (m, 1H), 4.26–4.28 (m, 2H); δ_{C} (150 MHz, CDCl_3) 170.1, 170.0(x2), 166.2, 165.3, 164.8, 140.3, 140.0(x2), 133.1(x2), 132.3, 128.1, 128.0, 127.7(x4), 127.5, 127.4, 127.1, 126.8, 125.3, 124.4, 123.7, 123.0, 122.9, 113.9(x2), 113.5, 113.1(x2), 112.9, 109.2, 107.6, 76.3, 75.8, 75.2, 66.8, 66.1, 63.8. ν_{\max} (cm^{-1}): 3448, 3061, 1617, 1583, 1541, 1468, 1455, 1442, 1396, 1347, 1265, 1225, 1152, 1078, 949, 931, 856, 756, 747, 728, 696, 593, 577, 545, 409. Elemental analysis for $\text{C}_{46}\text{H}_{38}\text{Cl}_2\text{N}_3\text{O}_6\text{Co}$ requires C: 64.34%, H: 4.46%, N: 4.89%; found: C: 64.48%, H: 4.27%, N: 4.90%.

Tri(ligand) manganese chelate (MnL1_3)

7. Tri(ligand) manganese chelate (MnL1_3) was prepared using the procedure described for compound **1** by refluxing a mixture of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2.5943 g, 10.59 mmol), 2-cyanophenol (2.3979 g, 20.13 mmol) and D-phenylglycinol (4.2681 g) in 40 mL of dry chlorobenzene for 60 h. The product was obtained as

dark brown crystals (3.2390 g) in 80% yield after evaporation from a mixture of ethanol and chloroform; m.p.: 138–142 °C, $[\alpha]_D^{25} = -36.72^\circ$ (c 0.488, CH₃OH), δ_H (600 MHz, CDCl₃, 27 °C) 7.75 (d, J=1.4 Hz, 2H), 7.29–7.43 (m, 21H), 6.89–7.07 (m, 4H), 5.46–5.48 (m, 2H), 4.87–4.88 (m, 2H), 4.23–4.34 (m, 2H), 3.71–3.81 (m, 3H); δ_C (150 MHz, CDCl₃), 165.8, 159.6, 141.1, 133.2, 128.4, 127.8, 127.4, 127.3, 126.6, 126.0, 118.3, 116.4, 110.0, 107.6, 73.6, 68.3; ν_{max} (cm⁻¹): 3431, 3061, 3026, 2966, 2913, 1617, 1543, 1454, 1402, 1350, 1268, 1231, 1115, 1085, 939, 864. Elemental analysis for C₄₅H₃₆N₃O₆Mn requires C: 70.22%, H: 4.71%, N: 5.46%; found: C: 70.03%, H: 4.93%, N: 5.35%.

PtL1(D-phenylglycinol)Cl

8. PtL1(D-phenylglycinol)Cl was prepared using the procedure described for compound **1** by refluxing a mixture of dry PtCl₂ (0.9026 g, 3.39 mmol), 2-cyanophenol (1.1959 g, 10.04 mmol) and D-phenylglycinol (4.3023 g). The three components were combined under water- and oxygen-free conditions in a dry 100 mL Schlenk flask. The components were dissolved in 80 mL of dry chlorobenzene, and the reaction mixture was refluxed for 60 h. The solvent was removed under reduced pressure, and the residue was dissolved in 15 mL of H₂O followed by extraction with dichloromethane (10 x 3 mL). The solvent was removed under vacuum to afford the crude product as a red oil. Further purification was carried out using silica gel chromatography (petroleum ether/dichloromethane 4/1) to obtain the desired product as red-brown crystals (1.6718 g) in 82% yield; m.p.: 146–148 °C, $[\alpha]_D^{25} = -24.19^\circ$ (c=0.0248, CH₃OH): ¹H NMR (300 MHz, CDCl₃, 27 °C), δ (ppm) = 7.25–7.48 (m, 13H), 6.77–7.01 (m, 1H), 4.81–4.92 (m, 1H), 4.73–4.76 (m, 2H), 4.23–4.65 (m, 1H), 3.96–3.99 (m, 1H), 3.67–3.69 (m, 3H); δ_C (75 MHz, CDCl₃): 159.9, 142.3, 140.2, 134.7, 129.5, 128.7, 128.6, 128.5, 128.4, 127.3, 119.8, 117.2, 74.6, 68.5, 64.9, 61.4. ν_{max} (cm⁻¹): 3210, 3124, 2876, 2161, 2035, 1615, 1584, 1535, 1494, 1454, 1399, 1365, 1306, 1255, 1194, 1056, 1018, 910, 838, 754, 694, 619, 575, 566. Elemental analysis for C₂₃H₂₂N₂O₃ClPt requires C: 45.59%, H: 3.83, N: 4.62%; found: C: 45.16%, H: 4.22%, N: 4.86%.

Conclusion

In conclusion, complexes **1–8** were obtained using a one-pot method with a sequential strategy [12]. The reaction outcome has been demonstrated for three-component reactions between metal salts, amino alcohols and 2-hydroxybenzonitrile to afford organometallic complexes in good yields (65%–95%). Additionally, the dimeric complex **3** and the trimeric complex **5** can be obtained by selection of the appropriate polar and nonpolar solvents. Investigations of the catalytic properties of these complexes as chiral ligands are currently ongoing. These complexes have exhibited bioactivities as anticancer reagents, and their future use in medical fields are currently under development.

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Supporting Information

Supporting information includes characterization spectra for compounds **1-8** as well as crystal structures and crystallographic information files (CIF). This material is available free of charge via the Internet at

Accession Codes: Complete crystallographic information files for all compounds have been deposited with the Cambridge Crystallographic Data Center as supplementary publications **CCDC 1035470-1035473, 1035475-1035476, 1035626 and 1835179**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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