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Chapter

One-Pot Synthesis of Chiral Organometallic Complexes

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Abstract

Currently, organometallic complexes involving ligand oxazolines are typically obtained in two sequential steps, where the free ligand is given firstly from a functionalized nitrile by condensation reaction with an amino alcohol in the presence of a Lewis or Bronsted acid catalyst, followed by a further coordination with metal salts to obtain the corresponding oxazolinyl metal complexes. Usually, the yield of the two-step procedure is relatively low; considering that metal oxazoline complexes often contain Lewis acidic metals, it is possible that the two steps may be telescoped. A series of novel chiral organometallic complexes (**1–23**) were assembled in a single step from nitriles, chiral D/L amino alcohols, and a stoichiometric amount of metal salts ($MCl_2 \cdot nH_2O/M(OAc)_2 \cdot nH_2O$), with moderate to high yields (20–95%). All the crystalline compounds were fully characterized by NMR, IR, MS, and X-ray analyses.

Keywords: chiral organometallic complexes, nitriles, amino alcohols, metal salts, crystalline compounds

1. Introduction

Chiral oxazolines constitute an important class of "privileged" ligands in asymmetric catalysis [1–8]. Organometallic complexes involving oxazoline ligands are typically obtained in two steps, where the free ligand is given firstly from a functionalized nitrile through condensation reaction with an amino alcohol in the presence of a Lewis or Bronsted acid catalyst, followed by further complexed coordination with metal salts to obtain the corresponding oxazolinyl metal complexes (**Figure 1**) [9, 10]. Usually, the yield of the two-step procedure is relatively low, and certain oxazolinyl organometallic complexes are difficult to obtain due to the poor coordination ability of the imine group from the oxazoline. It is conceivable that the two steps may be telescoped by using the requisite Lewis acid precursor. Herein, through the assembly of three reaction components (a nitrile, an amino alcohol, and metal salts), we first report a simple, one-step procedure for the preparation of N-containing heterocyclic zinc complexes (**1–15**), with the yield of certain products reaching 90% in the presence of a large amount of $ZnCl_2$ (0.4–2.6 eq.) and certain chiral salicyloxazoline metal complexes (**16–23**) with yields ranging from 65 to 95% using 1.0 eq. of copper, cobalt, nickel, manganese, palladium, and platinum salts as the third component. In all the cases, the complexes were isolated, purified, and characterized. All the structures reported in this paper were confirmed by X-ray crystallography.

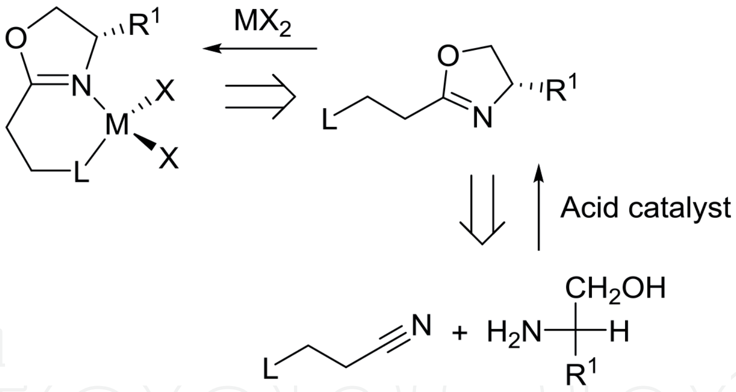


Figure 1.
Common method for the preparation of oxazolinyl metal complexes.

2. One-step multicomponent synthesis of chiral oxazolinyl-zinc complexes

The one-pot procedure was initially tested from the reaction of different 1-piperidine propionitrile derivatives with 2–3 eq. of amino alcohol refluxed in chlorobenzene for 72 h in the presence of 1–2.6 eq. of $ZnCl_2$. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was dissolved in H2O and extracted with CH_2Cl_2. The combined organic extracts were evaporated to give a crude red oil, which was purified by column chromatography (petroleum ether/CH_2Cl_2, 4/1) to afford the title compound as crystals. During the preliminary work, it quickly became apparent that the reaction results are controlled by the amount of $ZnCl_2$ used (**Figure 2**); for example, employing 1.1 eq. or 2.6 eq. of $ZnCl_2$, the desired crystal structures of the amino-oxazolidinyl zinc complex **1** and bis-oxazolidinyl zinc complex **2** containing two monodentate ligands can be obtained from the reaction of L-leucinol or L-valinol with 3-piperidin-1-yl-propionitrile, respectively, followed by evaporation of different ratios of petroleum and dichloromethane from the mixture after column separation but with only a low yield (25%) for complex **1** and moderate yield (65%) for complex **2**.

The nature of the side chain (R^1) influenced the reaction outcome. Using L-phenylalaninol with 1.6 eq. of $ZnCl_2$ or 1.5 eq. of $ZnCl_2$ with 1-morpholinepropionitrile (X = O) and D-phenylglycinol, both led to the cleavage of the propionitrile, providing asymmetric diamine complexes **3** and **4** at very good yields of 86% and 90%, respectively. Interestingly, using 1-(2-cyanoethyl)-4-methylpiperazine (Z = NMe) as a precursor with 2.5 eq. of $ZnCl_2$ led only to the formation of the zwitterionic piperazine complex **5**, irrespective of the amino alcohol used. The results again prove the effects of different amounts of metal salts on the reaction.

From the crystal structures of complexes **2–5**, we conclude that the propionitrile precursors are unstable and decompose into acetonitrile or the parent cyclic amines to afford complexes **2** and **3–5**, respectively, in the presence of a large amount of zinc chloride. For this reason, a number of nitrile precursors with additional N-donor were selected to be more robust against degradation under the reaction conditions. Consequently, a number of aromatic nitrile precursors containing additional N-donors were applied widely in these three-component reactions. In the process of selecting these reactions, the appropriate amount of $ZnCl_2$ was carefully optimized to ensure specific results. Complex **6**, listed in **Figure 3**, contains two monodentate ligands coordinated via the oxazoline nitrogen and was afforded from the use of 3-aminobenzonitrile and D-leucinol in the presence of 0.44 eq.

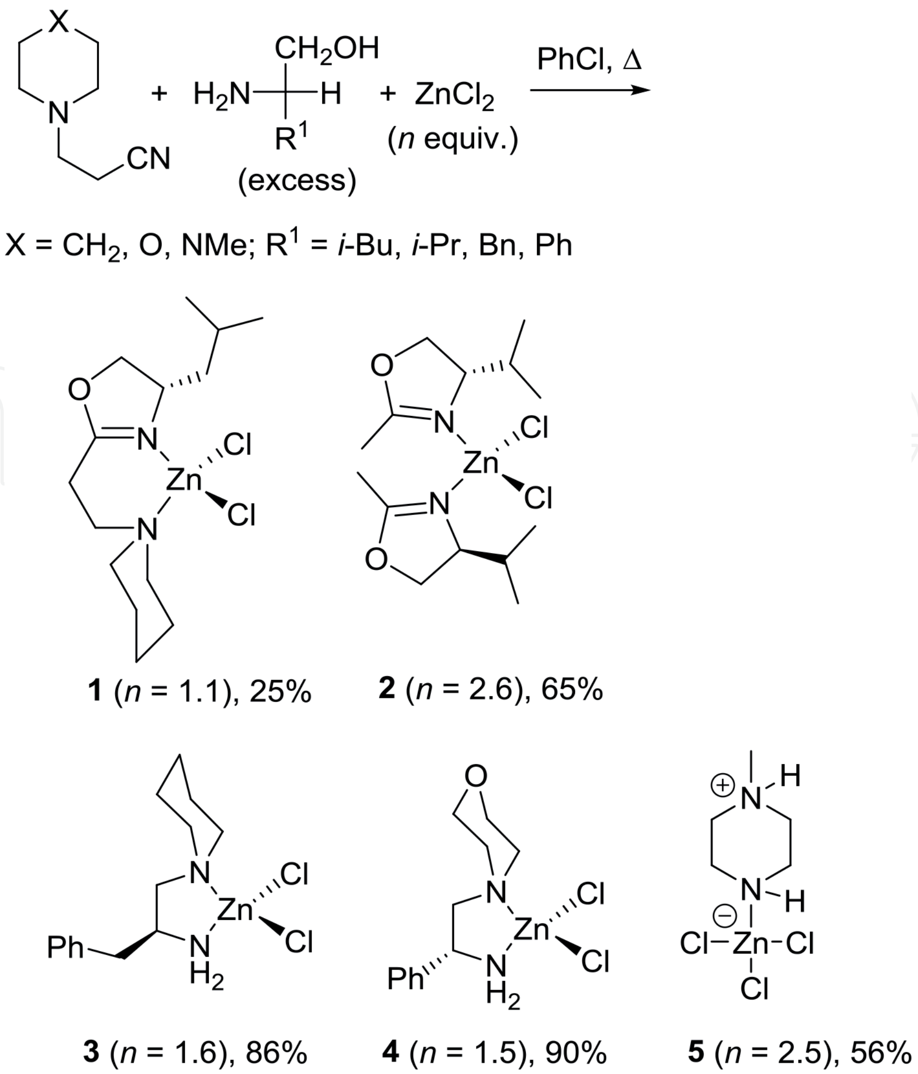
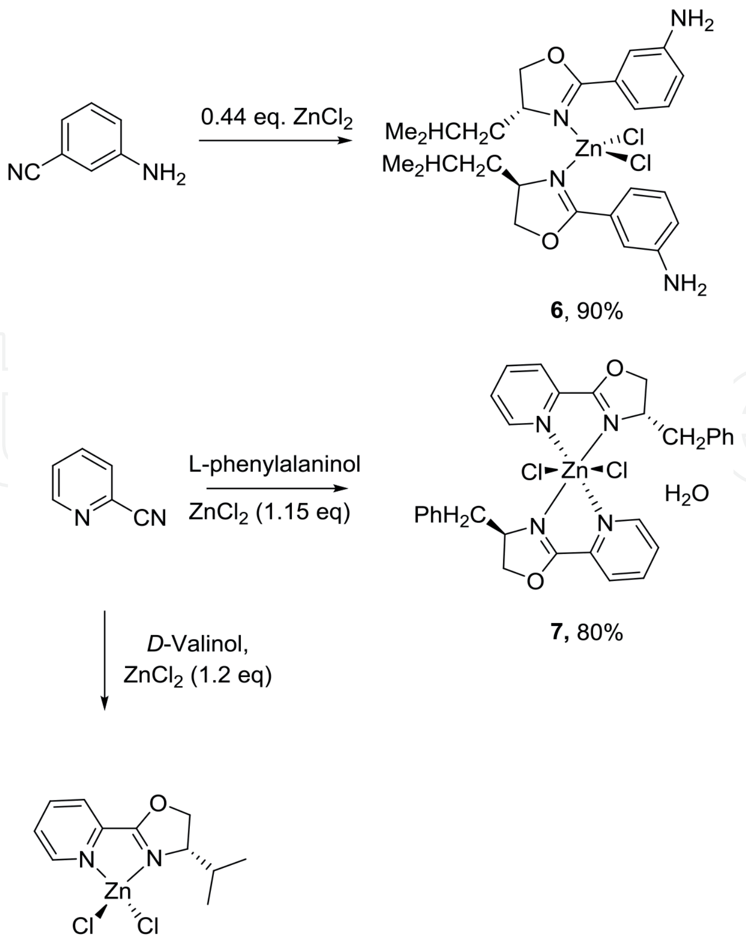


Figure 2.
Effect of the reaction stoichiometry of (metal precursor) $ZnCl_2$.

of $ZnCl_2$. Similarly, the bis-chelated complex **7** and the mono-chelated complex **8** were afforded to the corresponding yields of 80 and 78% from the use of 2-cyanopyridine with L-phenylalaninol and D-valinol, respectively, in the presence of 1.2 eq. of $ZnCl_2$.

The formation of complexes **9** and **10** were studied using different amino alcohols, as seen in **Figure 4**. C2-symmetrical bis-oxazolines formed seven-membered chelate rings which derived from 1,2-dicyanobenzene, affording a 1:1 adduct with zinc dichloride. Indeed, the addition of isophthalonitrile with D-phenylglycinol (0.56 eq.) provided the predicted mono-chelated complex **9** [11] at a good yield (68%). However, a combination of a slight excess of L-valinol (0.72 eq.) caused the addition of three amino alcohols to give complex **10** with a yield of 66%.

Surprisingly, the combination of L-leucinol and L-phenylglycinol with tetracyanoethylene in the presence of 0.42 eq. of $ZnCl_2$, respectively, provided neutral bis[bis(oxazoline)]zinc (II) complexes **11** and **12** with corresponding yields of 88 and 86% (**Figure 5**). The crystal structures of these methylene-bis(oxazoline) indicate that the tricyanomethane was formed as an intermediate from a disproportionation-rearrangement of the tetracyanoethylene precursor, although the precise mechanism of this pathway is unclear. In 2016, Kögel et al. reported the synthesis of complex **12** by a different route [12]. Interestingly, complex **12** was reported to exhibit an intense cotton effect as a result of exciton coupling. Indeed, the X-ray

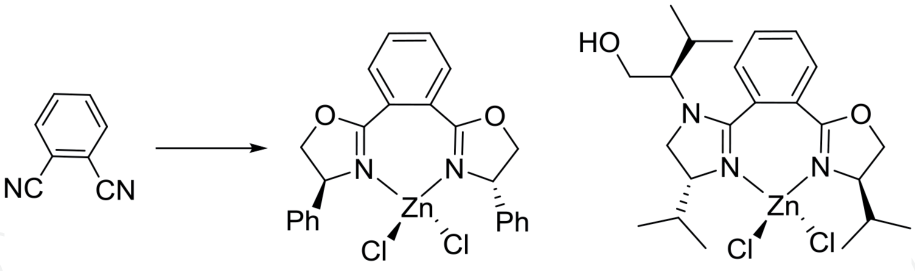


6, 90%

7, 80%

8, 78%

Figure 3.
*Zinc complexes **6–8** derived from 3-aminobenzonitrile and 2-cyanopyridine.*



9, 68%
x = 0.56 eq

10, 66%
x = 0.72 eq

Figure 4.
*Complexes **9–10** derived from isophthalonitrile.*

crystal structures of complexes **11** and **12** have been proven that due to the their coordination environments, isobutyl-substituted complex **11** has shown a fairly symmetrical tetrahedral comformation, while complex **12** is in highly distorted. This maybe the result of the favorable intramolecular π-interaction between one of the phenyl groups with the semicorrin structure of the adjacent ligand within 3.5 Å, effectively leading to the two chiral chromophores' close proximity to convenience exciton coupling [13].

In further study, 2-hydroxy-6-methylnicotinonitrile was employed as a precursor to test the applicability of the one-pot methodology in assembling complex multinuclear structures. In the presence of different amounts of $ZnCl_2$ (1.72, 1.31,

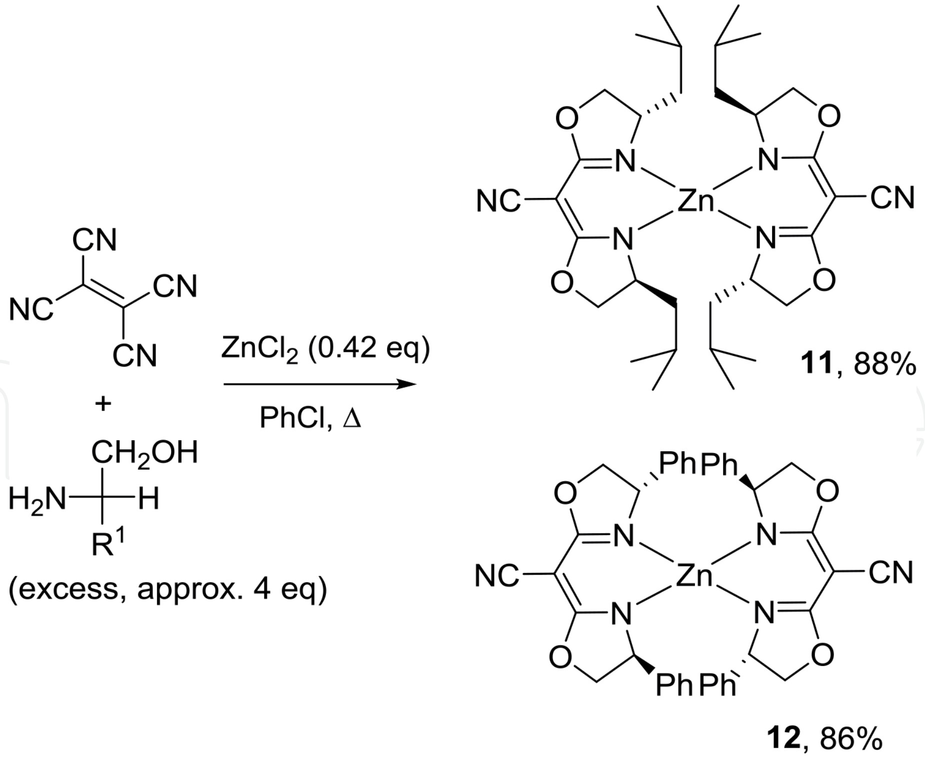


Figure 5.
Neutral zinc complexes derived from tetracyanoethylene.

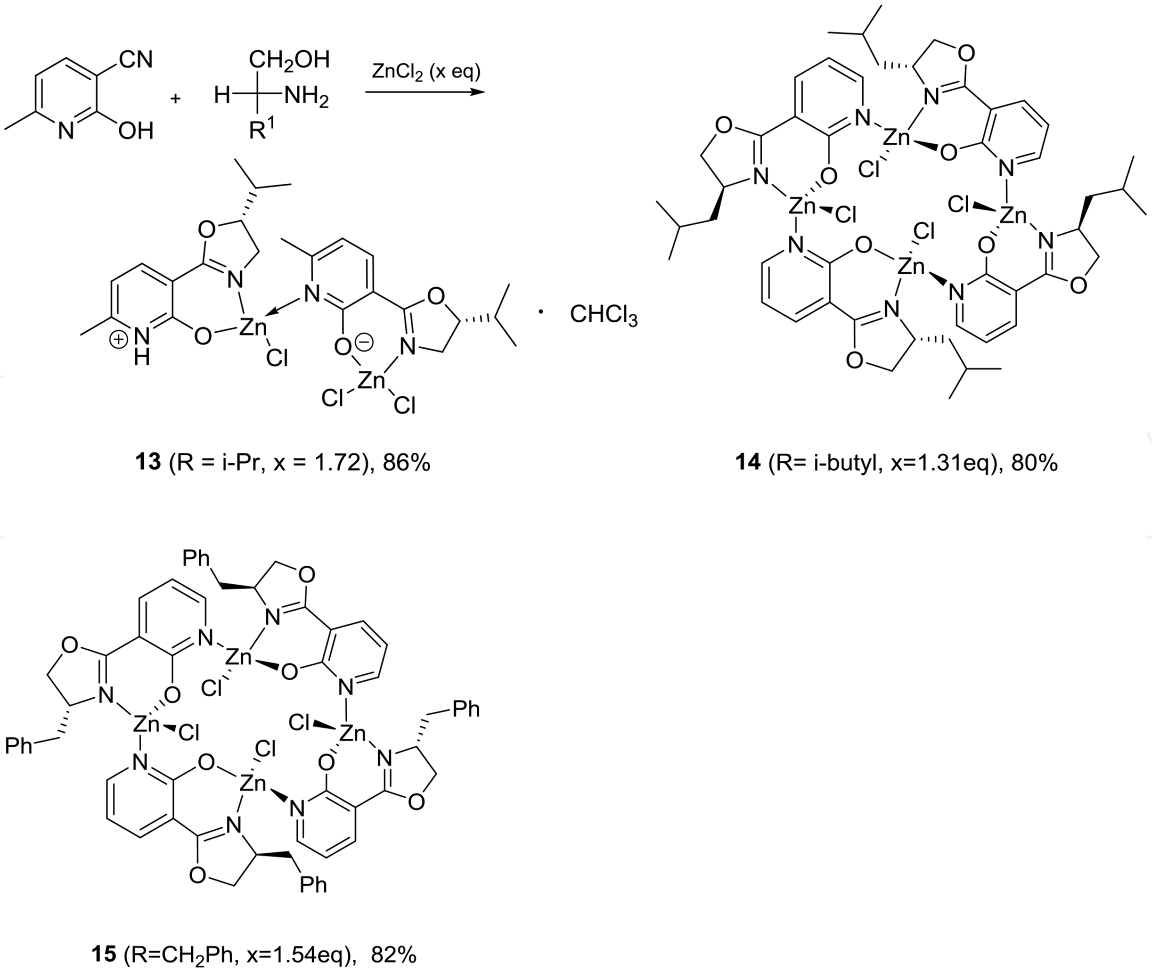


Figure 6.
*Multinuclear zinc complexes **13–15**.*

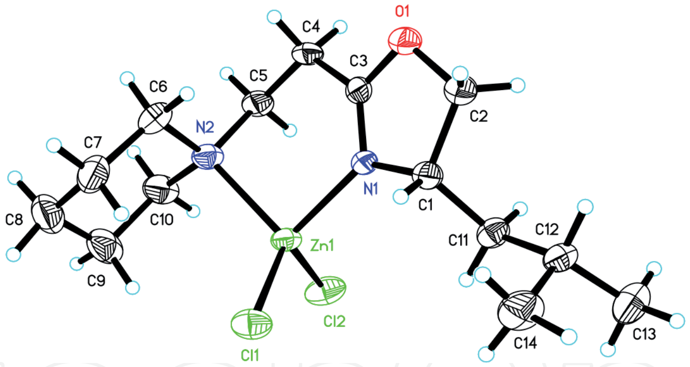


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Figure 7.
The crystal structure of complex 1.

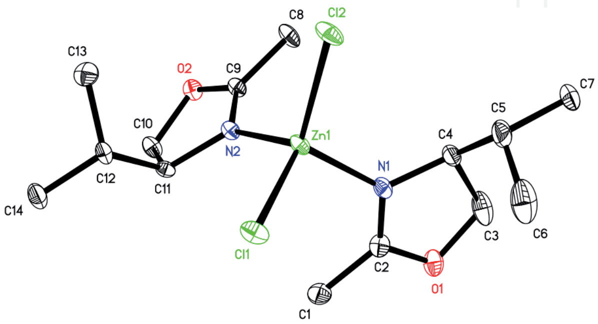

Figure 8.
The crystal structure of complex 2.

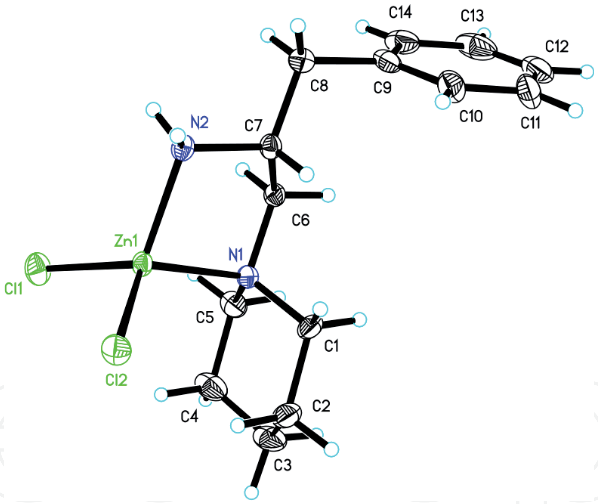

Figure 9.
The crystal structure of complex 3.

and 1.54 eq.), the corresponding condensation products with valinol, leucinol, or phenylalaninol furnished the binuclear zwitterionic complex **13** and highly symmetrical tetramers **14** and **15** at yields of 86, 80, and 82%, accordingly (**Figure 6**). Presumably, the formation of higher aggregates is prevented by the sterically demanding isopropyl substituents. A six-membered N,O-chelate ligand is complexed at each zinc metal center and connected to another metal center with a bridging donor ligand from the pendant pyridine. With each zinc atom located at a corner of a square grid, the planar N,O,N-ligands are oriented perpendicularly to one another with diagonal Zn···Zn distances of ca. 6 Å.

The crystal structures of all the complexes (**Figures 7–21**) are determined and reported by X-ray diffraction, elemental analysis, and IR. In all the cases, a distorted tetrahedral geometry is found at zinc(II), and the C═N double-bond character of the oxazolinyl ligand is largely retained in the metal complexes (**Table 1**).

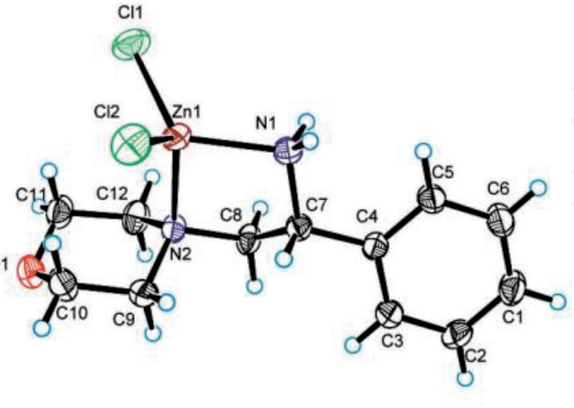

Figure 10.
The crystal structure of complex 4.

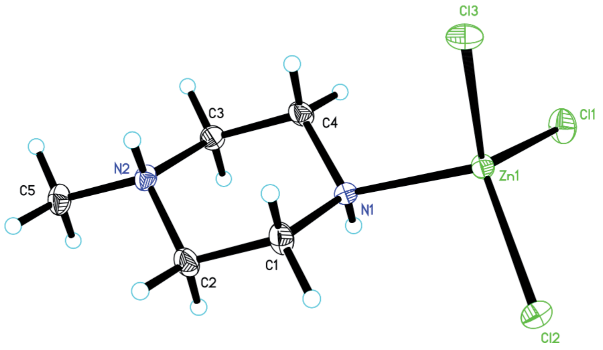

Figure 11.
The crystal structure of complex 5.

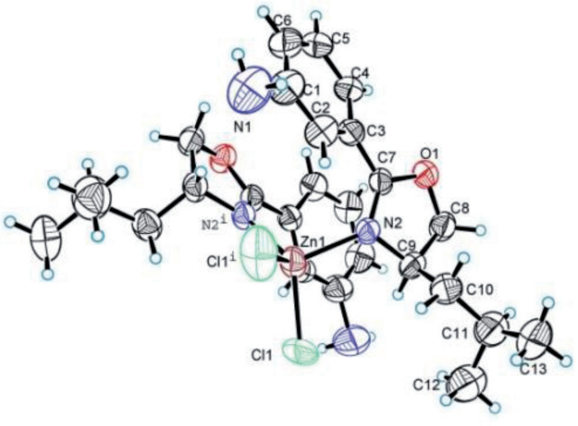

Figure 12.
The crystal structure of complex 6.

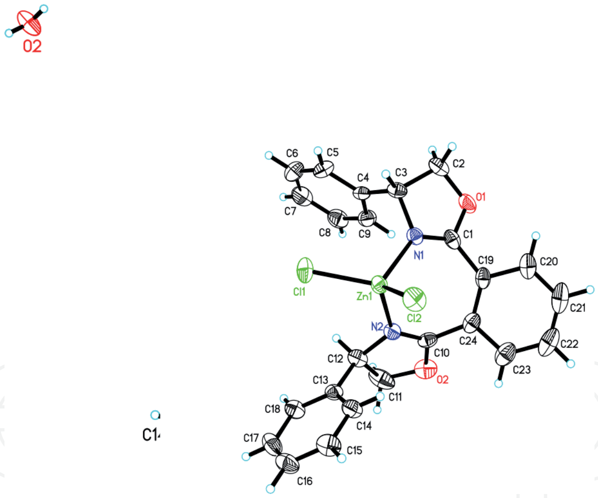

Figure 13.
The crystal structure of complex 7.

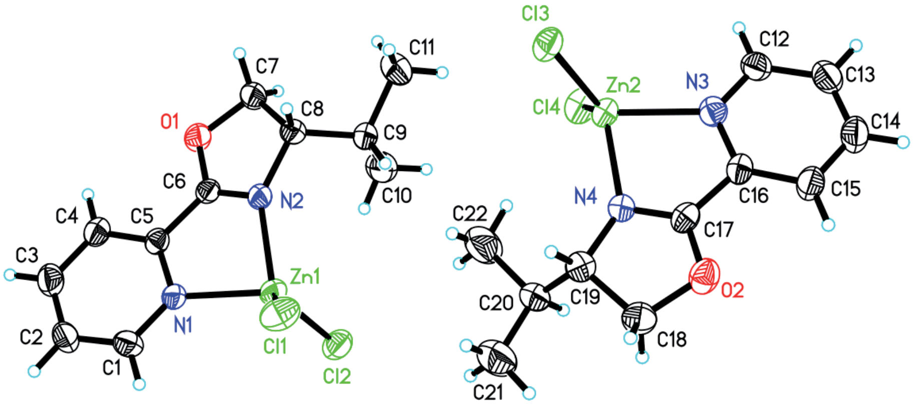

Figure 14.
The crystal structure of complex 8.

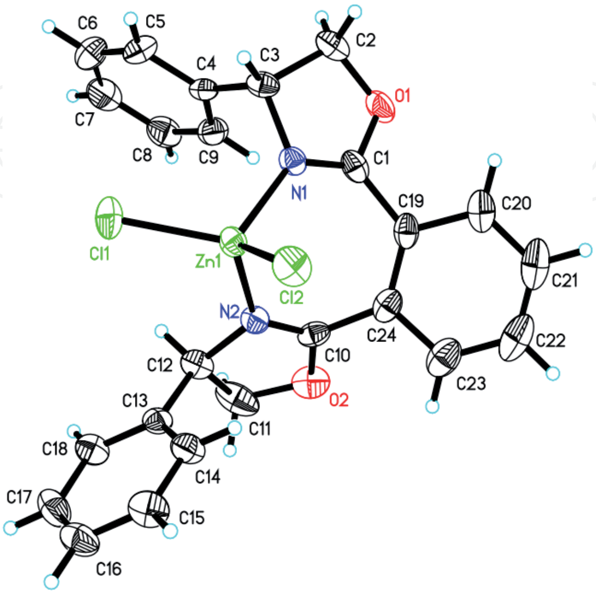

Figure 15.
The crystal structure of complex 9.

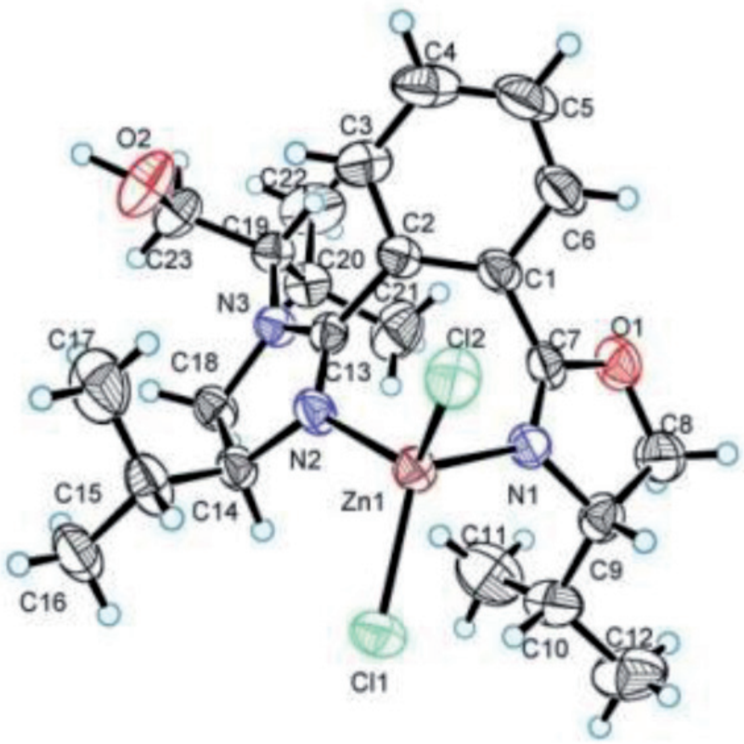

Figure 16.
The crystal structure of complex 10.

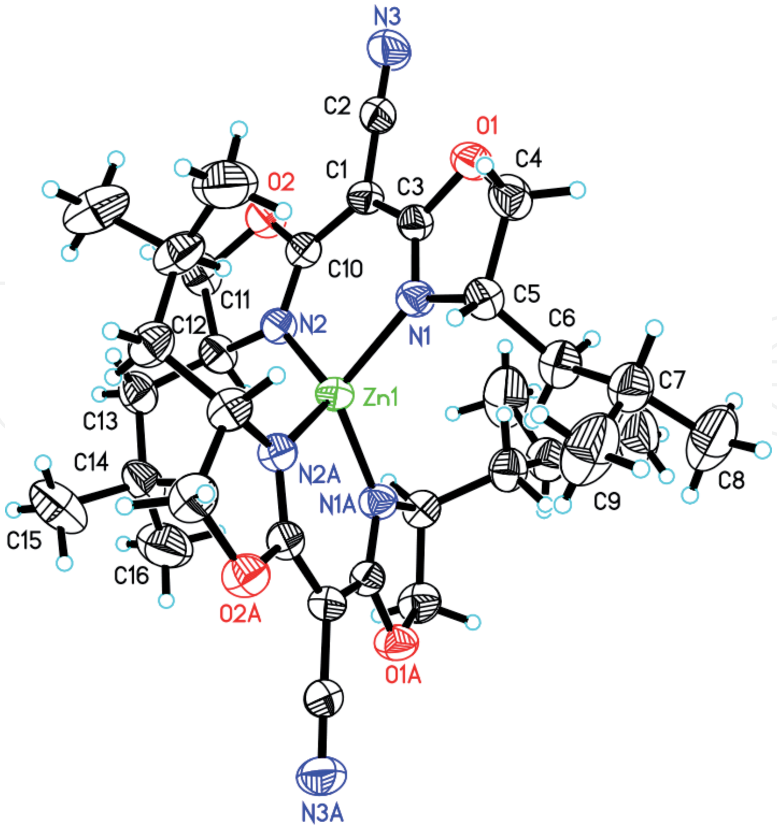

Figure 17.
The crystal structure of complex 11.

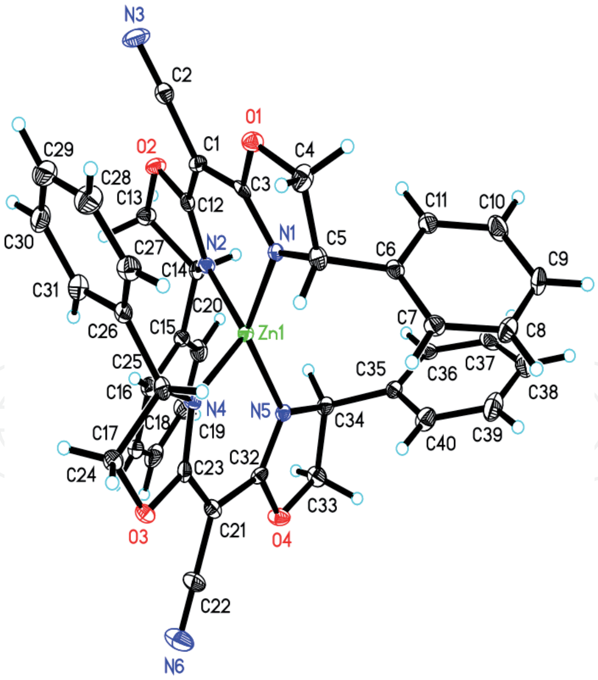

Figure 18.
The crystal structure of complex 12.

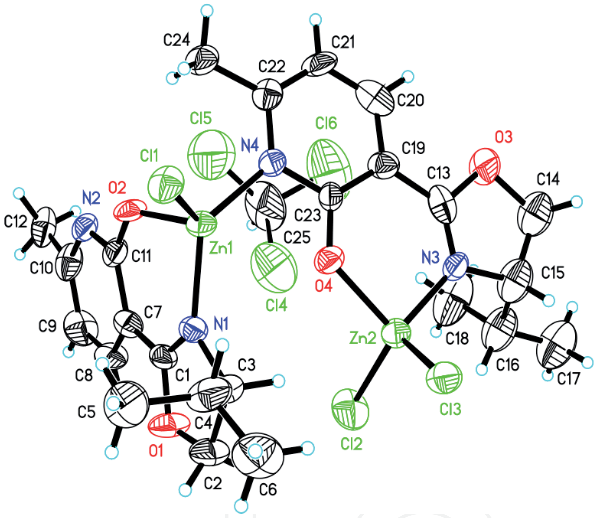

Figure 19.
The crystal structure of complex 13.

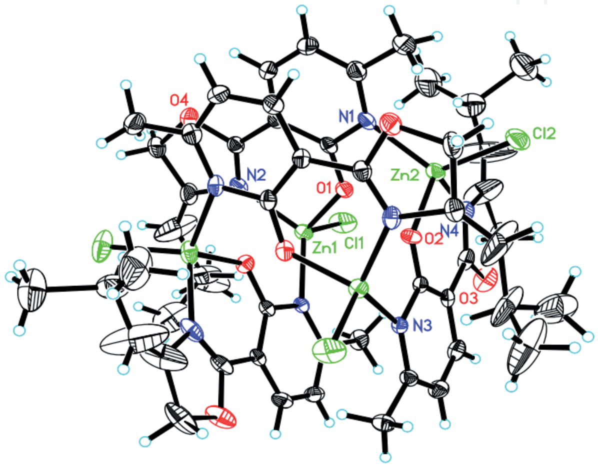

Figure 20.
The crystal structure of complex 14.

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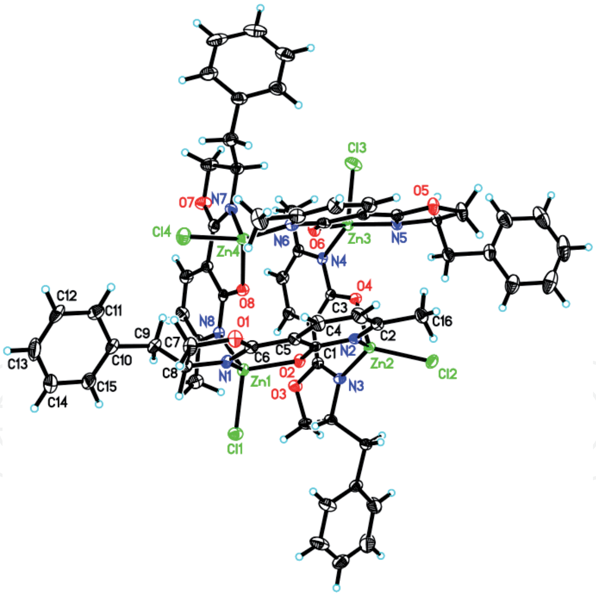

Figure 21.
The crystal structure of complex 15.

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ZnCl$_2$ (%)	Products	Yield (%)[a]
114.2	1	25
259.8	2	65
152.8	3	86
144.6	4	90
245.8–256.0	5	56
44.1	6	90
121.8	7	80
122.9	8	85
56.1	9	86
72.6	10	90
42.2	11	88
42.2	12	86
172.1	13	86
130.7	14	80
153.6	15	82`

[a]*Isolated yield from silica gel.*

Table 1.
One-pot synthesis of zinc complexes ***(1–15).***

3. One-step templated synthesis of chiral organometallic salicyloxazoline complexes

Chiral oxazolinyl organometallic complexes are very important catalysts in organic chemistry [14–22]. Several organometallic complexes containing 2-(2′-hydroxyphenyl) oxazolines are reported in the literature [23–42]. The general approach to the synthesis of metal complexes begins with ligand synthesis, followed by ligand reaction with metal salts to afford organometallic complexes [43].

In 2017, our research group first reported a one-pot multicomponent synthesis of chiral oxazolinyl-zinc complexes [44] in the presence of a large amount of $ZnCl_2$ (0.4–2.6 eq.); the yields of certain products reached 90%. Herein, the chiral salicyloxazoline metal complexes **16–23** can be obtained by using 1.0 eq. of metal salts such as copper, cobalt, nickel, manganese, palladium, and platinum salts as the third component. The structures of these complexes were characterized by X-ray crystallography. The results prove that organometallic complexes can be assembled with two reactants and different amounts of metal salts.

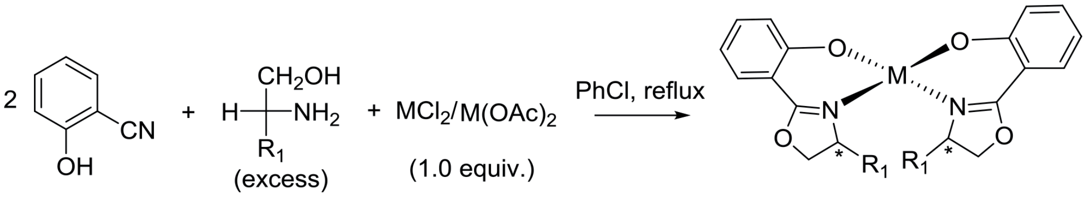
Chiral bis(oxazoline) copper complex **16**, nickel complex **17**, cobalt complex **18**, and palladium complex **19** were generated as crystals with the chemical formula ML_2 (L = 2-(4-R_1–4,5-dihydrooxazol-2-yl)phenol, R_1: D-Ph, M: Cu, Ni, Co; R_1: L-CH_2Ph; M: Pd). The syntheses of these complexes can be summarized as follows: A mixture of 2-hydroxybenzonitrile and D-phenylglycinol or L-phenylalaninol in 50 mL of chlorobenzene was refluxed for 72 h with 1.0 eq. of each of the above appropriate metal salts. After removal of the chlorobenzene, single crystals of chiral bis(oxazolinyl) metal complexes **16–19** were present after natural evaporation of the recrystallization or chromatographic solvent with petroleum and dichloromethane (**Figure 22**).

In **Figures 23** and **24**, refluxing a mixture of 2-cyanophenol and d-phenylglycinol in chlorobenzene for 72 h with 1.0 eq. of cobalt chloride hexahydrate or 1.0 eq. of cobalt acetate tetrahydrate, respectively, afforded complexes **20** and **21**. Further, through slow evaporation from a 1:1 mixture of ethanol and chloroform, crystals of complex **20** were obtained. However, the crystals of complex **21** were present after column separation with a 4:1 solution of petroleum ether and dichloromethane, followed by evaporation of the volatile components.

Notably, the product complexes **18** and **20** were obtained using $CoCl_2{\cdot}6H_2O$ as a reagent with different solvents in the workup procedure. As seen in **Figure 23**, when a nonpolar solvent, such as petroleum ether or n-hexane, was used in the recrystallization medium, crystals of complex **18** were obtained. However, if the recrystallization was carried out with a mixture of two polar solvents, such as ethanol and chloroform, crystals of complex **20** were obtained.

Similarly, in the synthesis of chiral oxazoline manganese complex **22** by the title method, 2-hydroxybenzonitrile and D-phenylglycinol were refluxed with 1.0 eq. of manganese acetate tetrahydrate in chlorobenzene for 60 h (**Figure 24**). After removal of the chlorobenzene and slow evaporation with a mixture of absolute ethanol and chloroform, crystals of complex **22** were obtained.

Interestingly, in **Figure 25**, when employed by 1.0 eq. of PtCl2 in the reaction of 2-hydroxybenzonitrile with D-phenylglycinol in chlorobenzene, the crystal structure of the resulting Pt complex was different from the aforementioned complexes **16–22** (**Figures 26–32**); a complex containing



16,17,18 R_1:D-Ph

16: $Cu(OAc)_2$, 65% or $CuCl_2$, 85%

17: $Ni(OAc)_2$, 92% or $NiCl_2$, 95%

18: $CoCl_2$, 72%

19: R_1:L-CH_2Ph; $PdCl_2$, 86%

Figure 22.
*Templated synthesis of complexes **16–19**.*

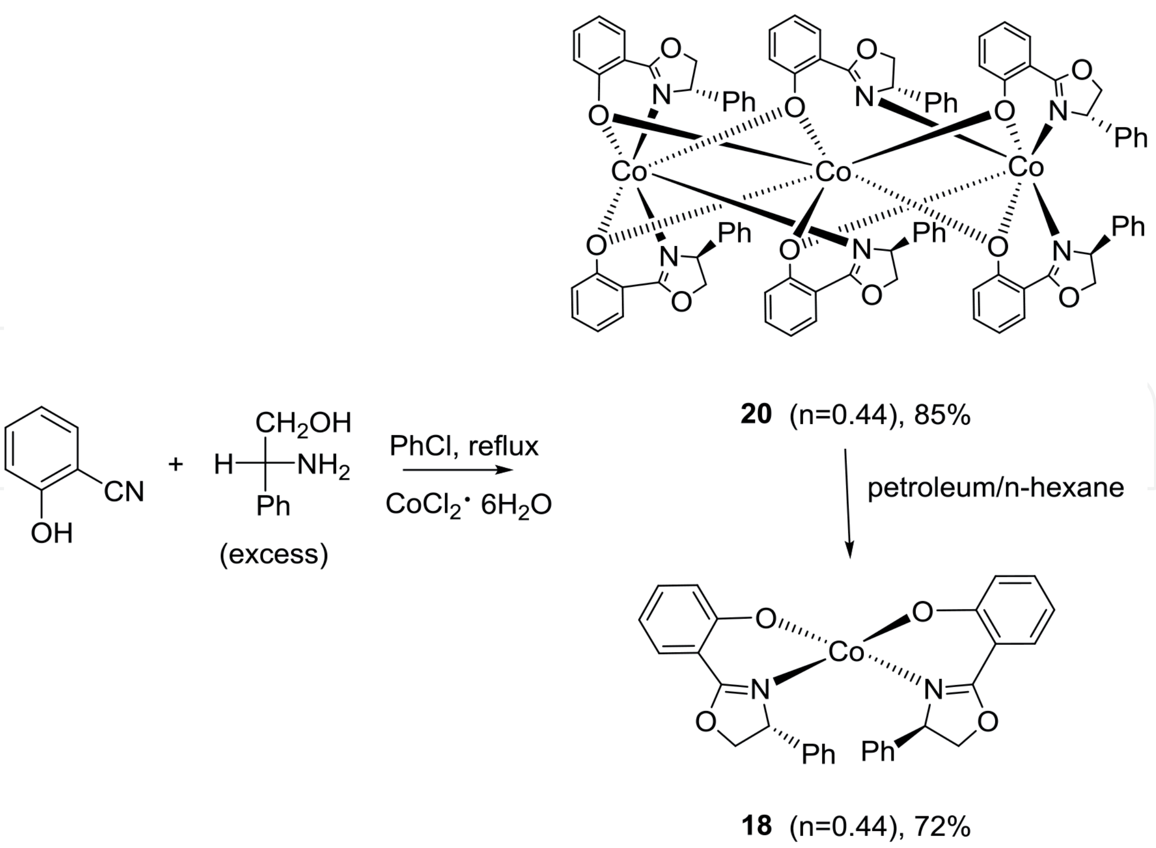


Figure 23.
*Solvent effects on the formation of complexes **18** and **20**.*

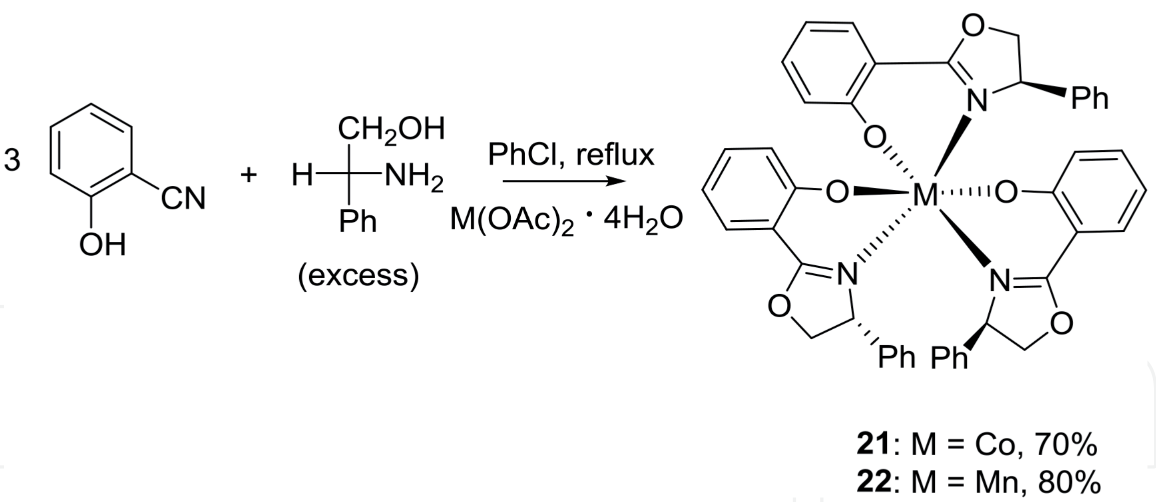


Figure 24.
*One-pot synthesis of tri(oxazoline) metal complexes **21** and **22**.*

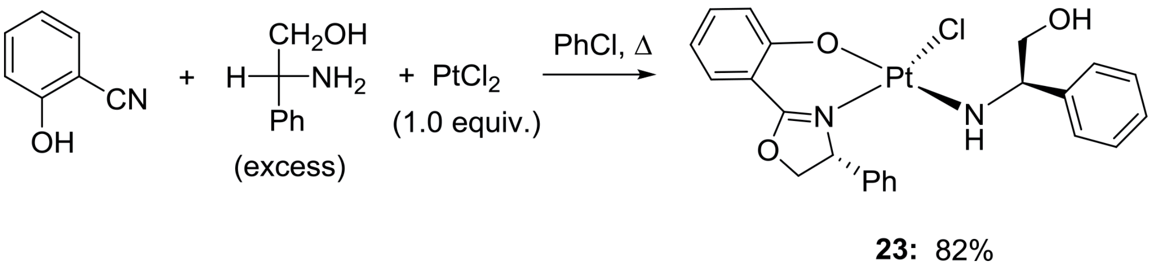


Figure 25.
*One-pot synthesis of oxazoline platinum complex **23**.*

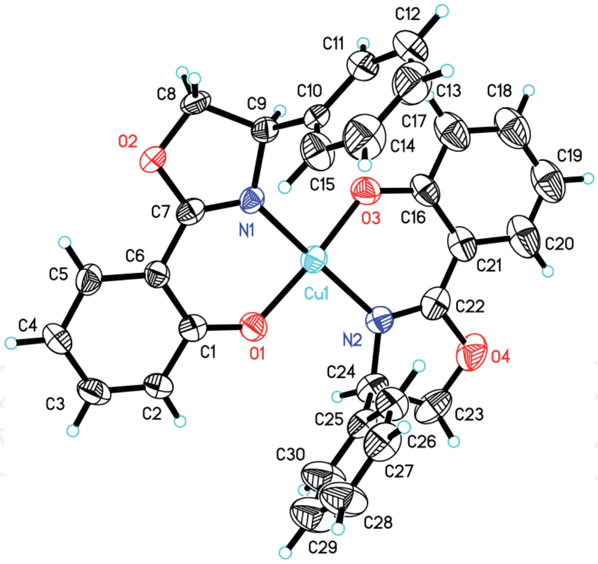


Figure 26.
The crystal structure of complex 16.

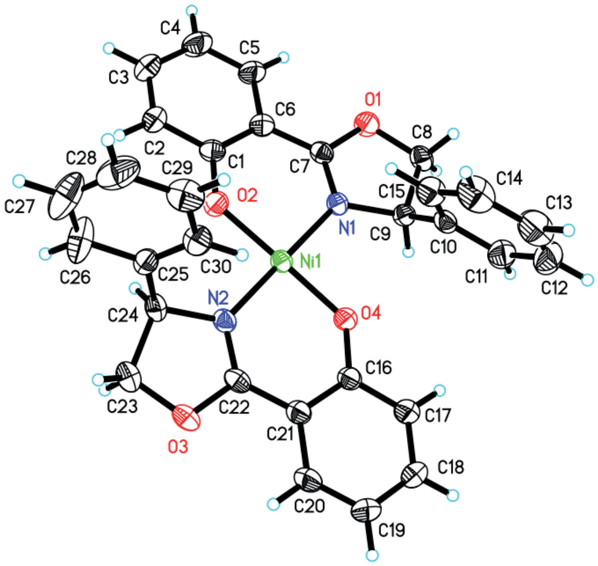


Figure 27.
The crystal structure of complex 17.

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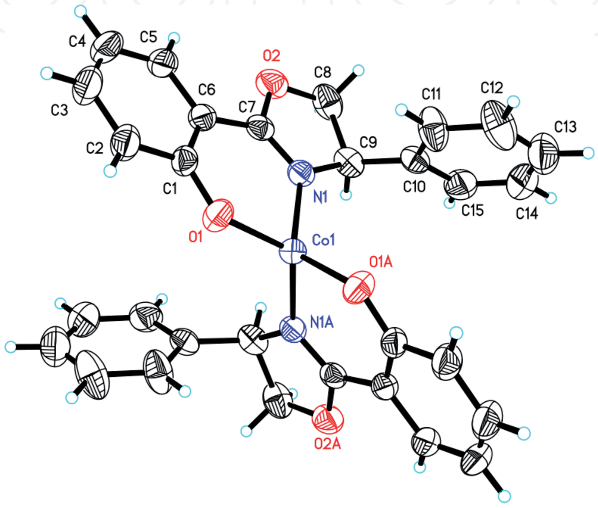

Figure 28.
The crystal structure of complex 18.

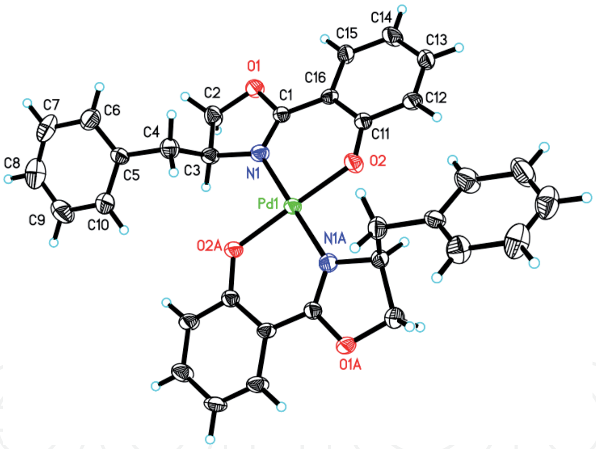

Figure 29.
The crystal structure of complex 19.

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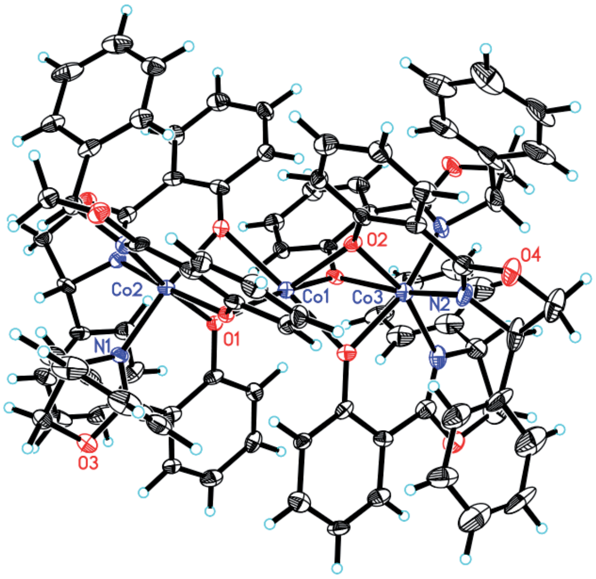

Figure 30.
The crystal structure of complex 20.

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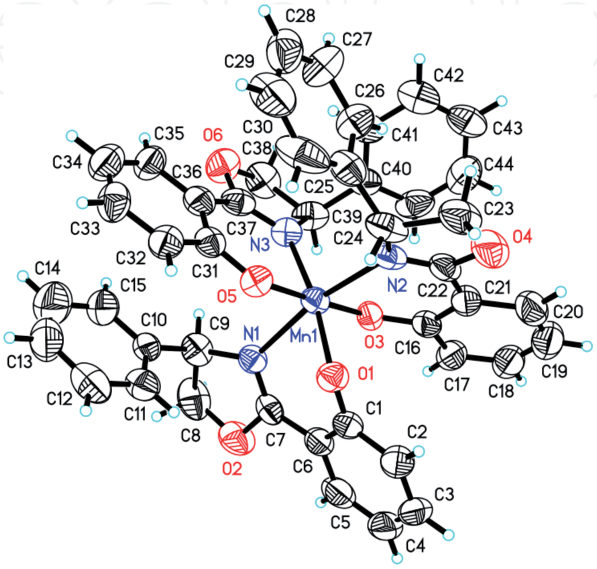

Figure 31.
The crystal structure of complex 21.

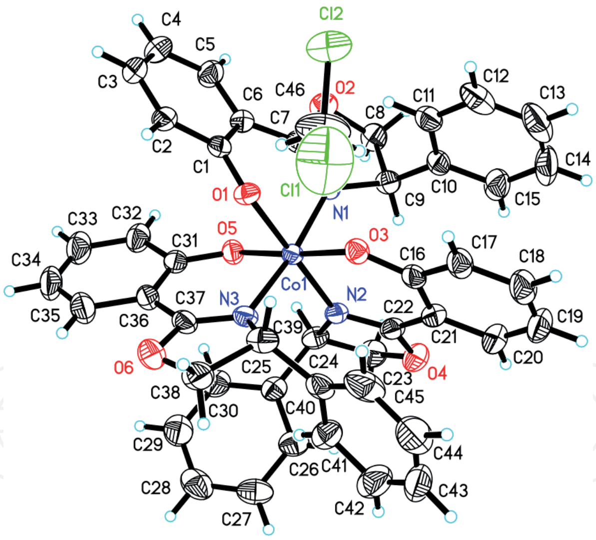

Figure 32.
The crystal structure of complex 22.

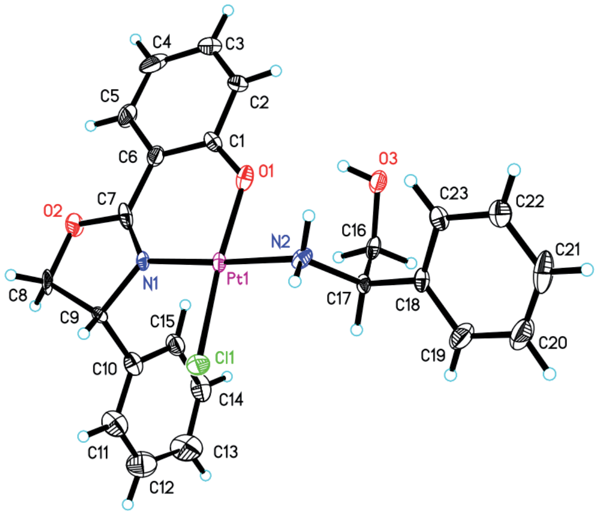

Figure 33.
The crystal structure of complex 23.

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Metal salts	The amount of metal salts	Products (%)	Yield (%)
$Cu(OAc)_2 \cdot H_2O$	55.7	16	65
$CuCl_2 \cdot 2H_2O$	53.2	16	85
$Ni(OAc)_2 \cdot 4H_2O$	51.0	17	92
$NiCl_2 \cdot 6H_2O$	53.0	17	95
$CoCl_2 \cdot 6H_2O$	44.3	18, 20	72, 85
$PdCl_2$	49.8	19	86
$Co(OAc)_2 \cdot 4H_2O$	42.3	21	70
$Mn(OAc)_2 \cdot 4H_2O$	52.6	22	80
$PtCl_2$	33.7	23	82

Table 2.
One-pot synthesis of salicyloxazoline complexes.

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 (**Figures 25** and **33**).

The proposed mechanism shows that excess metal salts can activate the reaction of 2-hydroxybenzonitrile with D-phenylglycinol in chlorobenzene to form ligand intermediates and then directly furnish the corresponding organometallic complexes via a one-step procedure (**Table 2**).

4. Conclusions

One-pot synthesis of oxazolinyl-zinc(II) complexes **1–23** at yields 25–95% was firstly demonstrated by assembling three-component reactions between metal salts, amino alcohols, and a variety of nitrile precursors. From the crystal structures of the complexes **1–23**, the reaction product is highly dependent on the presence of ligands, the amount of metal salts, and the nature of the substituent at the stereogenic center, giving a variety of coordination modes, such as mono- and bis-chelate complexes, mononuclear and mutinuclear complexes, etc.

Investigations into other oxazolinyl organometallic complexes and the catalytic properties of these complexes as chiral ligands are currently ongoing. These complexes exhibit bioactivities as anticancer reagents, and the future use of these complexes in medical fields is currently being developed.

Acknowledgements

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Conflicts of interest

The authors declare that they have no competing interests.

Appendix

Additional information is provided in the article as follows:

1. The characterization spectra of compounds **1–15** [44] are available free of charge via the Internet at https://ccj.springeropen.com/. The crystallographic information of compounds **1–15** are available from the Cambridge Crystallographic Data Center (CCDC) as supplementary publications CCDC 853709–853,710, 931,745–931,746, 931,745–931,748, 931,751–931,753, 931,756, 1,014,806–1,014,807, and 1,540,756, deposit@ccdc.cam.ac.uk or http://www. ccdc.cam.ac.uk.

2. Supporting information including the NMR spectra for compounds **1–15** [44] are available free of charge via the Internet at https://ccj.springeropen.com/articles/10.1186/s13065-017-0305-1.

3. Supporting information including the NMR spectra for compounds **16–23** [45] are available free of charge via the Internet at: Crystallographic Data Center (CCDC) as supplementary publications CCDC 853709–853710, 931745–931746, 931745–931748, 931751–931753, 931756, 1014806–1014807 and 1540756.

4. The crystallographic information of compounds **1–23** are available from the Cambridge Crystallographic Data Center (CCDC) as supplementary publications CCDC 853709–853,710, 931,745–931,746, 931,745–931,748, 931,751–931,753, 931,756, 1,014,806–1,014,807, 1,540,756, and CCDC 1035470–1,035,473, 1,035,475–1,035,476, 1,035,626, and 1,835,179, deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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