Predetermined Chirality at Metal Centers of Various Coordination Geometries: A Chiral Cleft Ligand for Tetrahedral (T-4), Square-Planar (SP-4), Trigonal-Bipyramidal (TB-5), Square-Pyramidal (SPY-5), and Octahedral (OC-6) Complexes

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Abstract: Two tetradentate bis-pinene–bipyridine type ligands, each with six stereogenic carbon centers, were synthesized from (−)-α-pinene. Their ability to predetermine chiral configurations at metal centers was studied. The two diastereoisomers, **L1** and **L2**, differ in their absolute configuration at the bridgehead position. These ligands form metal complexes with Ag^{I}, Pd^{II}, Zn^{II}, Cu^{II}, and Cd^{II}, with coordination numbers four, five, and six and with complete control of chirality at the metal centers. Using **L1** rather than **L2** leads to complexes of inverted absolute configuration at the metal centers. These diastereomeric coordination species can be obtained either as separate compounds or, in some cases, as solids containing them in a 1:1 ratio. Ligands **L1** and **L2** thus show that the pinene–bipyridines are versatile molecules for the formation of metal complexes with predetermined chirality. In all cases, absolute configurations were determined in the solid state by X-ray diffraction methods and in solution by CD spectroscopy. The sign of exciton couplets from the $\pi-\pi^*$ transitions always agrees with the expectations for a given local configuration at the metal center. The five-coordinate, inherently chiral species of Zn^{II} and Cu^{II} described in this article are the first examples of trigonal-bipyramidal metal complexes with predetermined absolute configuration containing topologically linear ligands.

Keywords: chirality · coordination chemistry · diastereoselective synthesis · N ligands · stereochemistry

Introduction

Stereoselective synthesis of metal complexes was previously introduced by Smirnoff and Werner in 1919. However, it has remained a somewhat neglected subject that has not been studied to a comparable degree as in organic chemistry. There, the synthesis of natural products has made it imperative to develop many stereoselective synthetic methods, especially for the generation of controlled configurations at carbon centers. In view of the highly variable coordination numbers and geometries of metal centers in coordination compounds, control of the absolute configuration is a rather formidable task in molecular engineering. Recent progress in various fields of coordination chemistry, such as self-assembly,[1, 2] enantioselective catalysis,[3, 4] and the synthesis of multicenter functionalized complexes[5] has stimulated interest in this field. A review of the development of diastereoselective synthesis with the aim of predetermination of absolute configurations at metal centers in coordination chemistry was published recently.[6] Here we present a series of results obtained with two diastereoisomers of a new ligand of the *Chiragen*[7, 8] family: *(−)-5,6-Chiragen[0] (R,R,S)* (**L1**), and *(−)-5,6-Chiragen[0] (R,R,R)* (**L2**)(Scheme 1).

In the *Chiragen* type ligands, two pinene–bipyridine moieties are connected in such a way as to produce a tetradentate ligand, which is, from a topological point of view, linear. The pinene part is attached to the bipyridine (bpy) in either the 4,5 or 5,6 position and the bridge [-B-] can be varied using xylyl or alkyl spacers, for example.

If the two pinene–bpy moieties are directly connected, the ligand is called *Chiragen[0]*.[9] Since the *Chiragen* ligands have been shown to predetermine the chirality at metal centers in mononuclear and polynuclear species, as well as in circular,[10] linear,[11] or infinite[12] helicates, we investigated the ability of these new ligands to control the chirality at metal centers (Figure 1). The *(−)-5,6-Chiragen[0]* ligands possess two bind-

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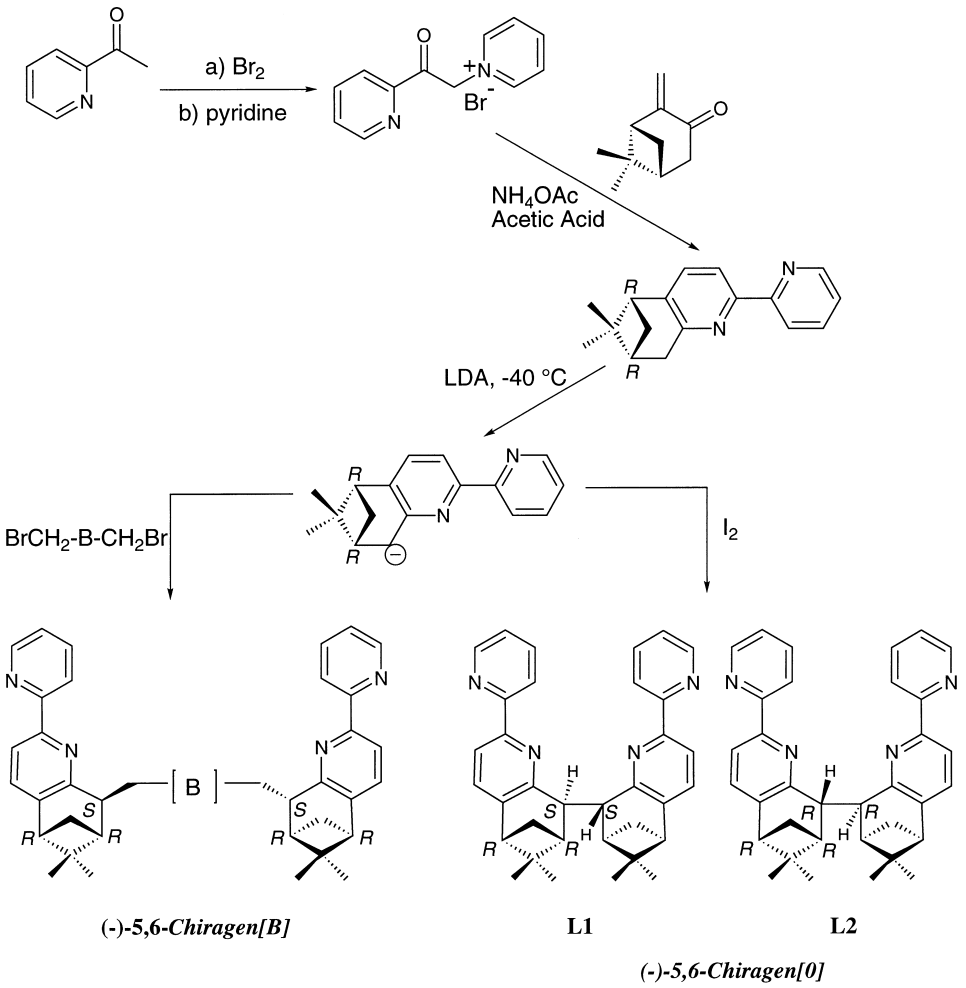
ing domains, which are disposed in such a way as to make the simultaneous coordination to two metal centers very unlikely. Therefore, coordination of the ligand to mainly one metal center is to be expected. In order to probe the steric control of these ligands, metals exhibiting various coordination numbers and geometries were tested.

Results and Discussion

Synthesis and characterization of the ligands: As has been described previously, *Chiragen* ligands are prepared by using the sequence of reactions given in Scheme 1. It has been shown in several cases that the connection through a bridge between the pinene–bpy units occurs in a highly stereoselective manner.[7] In the example shown, the bridgeheads are *S,S*-configured. If the deprotonated species obtained using lithium diisopropylaminde (LDA) is treated with I_2, direct oxidative coupling of the two pinene–bpy units occurs. However, stereoselectivity is not quantitative in this case. Two diastereoisomers, **L1** (*R,R,S)* and **L2** (*R,R,R)*, are formed in a ratio of 10:1. The formation of two



Scheme 1. Synthetic pathway for the Chiragen type ligands containing a bridge: (−)-5,6-*Chiragen[B]* or connected directly: *(−)-5,6-Chiragen[0]*.

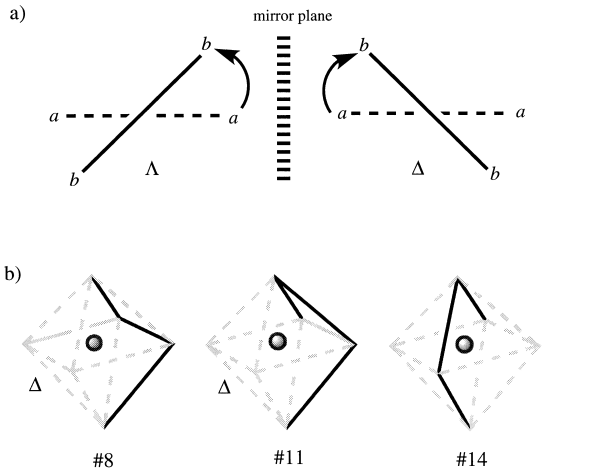


Figure 1. a) Skew line system for the chirality descriptors Δ and Λ in nonoctahedral complexes. The ligands are projected onto lines. b) The possible configurations of a complex in octahedral geometry containing a bis-bidentate ligand.

Abstract in German: *Ausgehend von (−)-α-Pinen, wurden zwei neue tetradentate bis-Pinen-Bipyridin Liganden synthetisiert und deren Tauglichkeit zur Prädetermination der chiralen Konfiguration an Metallzentren untersucht. Die beiden diastereomeren Liganden **L1** und **L2** unterscheiden sich durch die absolute Konfiguration des Zentrums am Brückenkopf des Moleküls. Mit **L1** und **L2** konnten unter vollständiger Kontrolle der Chiralität Komplexe der Metallzentren Ag^{I}, Pd^{II}, Zn^{II}, Cu^{II} und Cd^{II} mit den Koordinationszahlen vier, fünf und sechs erhalten werden. Die diastereomeren Liganden bilden meist ebensolche Komplexe, welche in reiner Form dargestellt werden können, in anderen Fällen bilden sich Verbindungen, die einer stöchiometrischen 1:1 Zusammensetzung beider Formen entsprechen. Die Liganden **L1** und **L2** zeigen somit, dass Pinen-Bipyridine in vielfältiger Art und Weise zur Bildung von Metallzentren mit prädeterminierter Konfiguration eingesetzt werden können. Die absoluten Konfigurationen der Metallzentren wurden durch Röntgendiffraktion im Festkörper, beziehungsweise durch CD-Spektroskopie in Lösung bestimmt. Das Vorzeichen der Signale, die den Exciton gekoppelten π-π* Übergängen zugeordnet werden können, stimmt in allen Fällen mit den erwarteten lokalen Konfigurationen an den Metallzentren überein. Die fünfach koordinierten, inhärent chiralen Komplexe von Zn^{II} und Cd^{II}, sind die ersten Beispiele prädeterminierter absoluter Konfiguration an trigonal-bipyramidalen Zentren mit topologisch linearen Liganden.*

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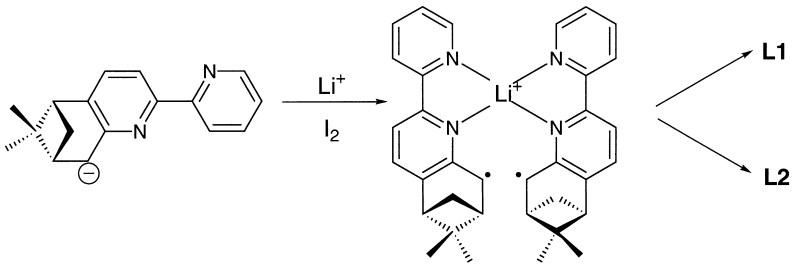
differently configured bridgeheads indicates that the oxidative coupling of the two pinene–bpy moieties occurs via a radical intermediate (Scheme 2) as opposed to the nucleophilic substitution with the dibromo compounds employed for *Chiragen* ligands having a bridge. However, it is surprising



Scheme 2. Radical mechanism of the reaction leading to a mixture of **L1** and **L2**.

that the decreased configurational stability of the radical, as compared with the carbanion, does not yield the mixed *R,R,S*-*R,R,R* diastereoisomer in a statistically preferred ratio. Model studies show that coupling most probably occurs via a template complex, where Li^+ (introduced through LDA) coordinates to two bpy units.[13] In this template (Scheme 2), both the *R,R,R* and *R,R,S* configurations are sterically feasible, whereas the *R,R,S*-*R,R,R* is highly disfavored.[*]

Both *5,6-Chiragens[0]* **L1** and **L2** formed crystals (see Table 1) suitable for X-ray diffraction, yielding the molecular structures shown in Figure 2.

In the more abundant **L1**, as expected, the two pyridine rings of each bipyridine unit are in the transoid conformation[14] (dihedral angle is 10.4°) and the angle between the planes of the two pyridine rings connected by the pinene groups is 78.6°. A C_2 crystallographic axis, bisecting the C13–C13′ bond is present.

[*] The *R,R,S*-*R,R,R* isomer can be formed in small quantities by adding tetramethylethylenediamine (TMEDA) to the reaction mixture before the oxidative coupling. The TMEDA will complex Li^+ ions and the template effect no longer occurs.

Abstract in Romanian: *Doi liganzi diastereoizomeri (**L1** şi **L2**) de tip bis-pinen-bipiridină au fost sintetizaţi utilizând (−)-α-pinen în scopul de a studia capacitatea lor de a predetermina chiralitatea centrilor metalici. Fiecare ligand posedă şase centrii de carbon stereogenici dintre care doi au o configuratie inversă comparativ cu celălalt diastereoizomer. **L1** si **L2** au fost complexaţi cu ioni metalici: Ag^I, Pd^{II}, Zn^{II}, Cu^{II}, Cd^{II}, având numere de coordinatie diferite: patru, cinci, şase. Chiralitatea centrilor metalici din combinaţiile complexe obţinute este indusă de chiralitea ligandului: ligandul **L1** impune centrului metalic o chiralitate Δ în timp ce ligandul **L2** obligă ionul metalic să adopte configuraţia inversă Λ. În toate cazurile configuraţia absolută a centrilor metalici a fost determinată în stare solidă prin difracţie de raze X şi în soluţie prin spectroscopie DC (dicroism circular). Combinaţiile complexe ale zincului (II) si cuprului (II) cu număr de coordinaţie cinci, descrise în prezentul articol, sunt primele exemple de complecşi metalici cu configuraţii absolute controlate de către liganzi lineari din punct de vedere topologic.*

In the **L2** isomer, the C_2 crystallographic axis is no longer present, yielding two dihedral angles for the two pyridine rings of each bipyridine moiety (8.9° and 2.9°, respectively). The angle between the planes of the two pyridine rings connected by the pinene groups is 33.7°. This difference in the conformation of the two ligands with respect to rotation about the C13–C13′ bond is most probably due to steric hindrance.

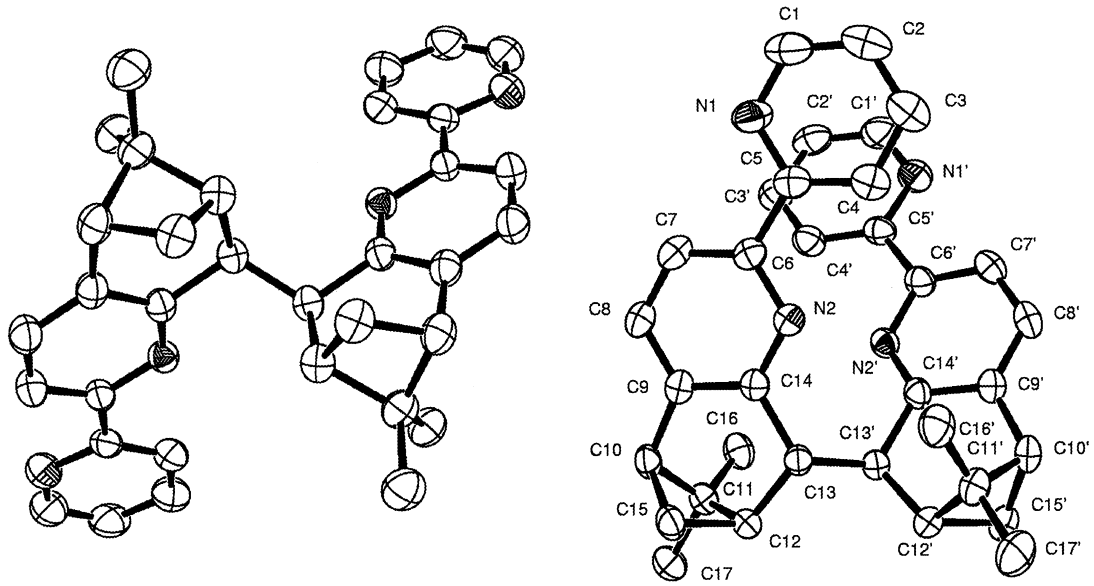
In the ^{1}H NMR spectrum (Table 2) the two protons at the bridgeheads (C13) appear as singlets and are shifted to low field compared with the corresponding protons of bridged *Chiragens,* for instance *(−)-Chiragen-5,6-[p-xyl]*.[10] This shift is large for the *R,R,S* isomer ($\Delta\delta = 1.16$ ppm) and small in the case of *R,R,R* isomer ($\Delta\delta = 0.18$ ppm). The methyl groups in **L1** have signals comparable to those of bridged *Chiragens,* whereas those in **L2** show a distinct low field shift ($\Delta\delta = 0.73$ ppm) for the methyl group C16.

CD spectra of **L1** and **L2** are remarkably different (Figure 3). In contrast to *Chiragen* ligands having a bridge between the pinene–bpy moieties, they show significant CD signals in the region of the $\pi-\pi^*$ transitions of the bpy groups

Table 1. X-ray crystallographic data collection and refinement details for **L1** and **L2**.

	L1	**L2**
formula	$C_{34}H_{34}N_4$	$C_{34}H_{34}N_4$
mol. weight	498.65	498.65
crystal appearance	colorless rods	colorless blocks
crystal system	monoclinic	orthorombic
space group	*I*2	$P2_12_12_1$
a [Å]	13.0151(13)	8.9165(6)
b [Å]	6.1910(4)	17.0668(11)
c [Å]	16.9432(16)	17.7943(12)
α [°]	90	90
β [°]	92.815(12)	90
γ [°]	90	90
volume [Å^3]	1363.6(2)	2707.9(3)
Z	2	4
ρ [g cm^{-3}]	1.214	1.223
μ [mm^{-1}]	0.072	0.072
crystal size [mm]	0.70 × 0.10 × 0.05	0.45 × 0.40 × 0.40
temperature [K]	223(2)	223(2)
radiation [Å]	$Mo_{K\alpha}$ ($\lambda = 0.71073$)	$Mo_{K\alpha}$ ($\lambda = 0.71073$)
scan type	φ oscillation	φ oscillation
θ max [°]	$3.13 < \theta < 25.86$	$2.39 < \theta < 25.92$
measured reflections	5383	18043
independent reflections	2588	5230
observed reflections	1835, $I \le 2\sigma(I)$	4555, $I \le 2\sigma(I)$
R[a]	0.0289	0.0279
wR_2[b]	0.0553	0.0654
R[a] (all data)	0.0493	0.0342
wR_2[b] (all data)	0.0595	0.0674
absolute structure param.	0.0(2)	−0.1(15)

[a] R factor definition: $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] SHELXL-97 wR_2 factor definition: $wR_2 = [\Sigma w(F_o^2 - F_c^2)2/\Sigma w(F_o^4)]1/2$. Weighting scheme: $w = 1/[\sigma^2(Fo)^2 + (np)^2 + 0.00p]$, $p = (\max(F_o^2) + 2F_c^2)/3$.



L1 **L2**

Figure 2. ORTEP representations of the ligands **L1** and **L2**. Hydrogen atoms are omitted for clarity.

Table 2. Comparison of the chemical shifts of protons in L1, L2, and the bridged ligand (−)-Chiragen 5,6-[*p*-xyl].[11] The presence of one half of the total protons is consistent with C_2-symmetry.

Ligands	Chemical shift of the protons (ppm)												
	1	2	3	4	7	8	10	12	13	15a	15b	16	17
L1	8.61	7.21	7.71	8.33	8.10	7.34	2.78	2.13	4.58	1.38	2.49	0.76	1.30
L2	8.27	6.94	7.30	7.09	7.88	7.37	2.84	2.65	3.6	1.33	2.79	1.36	1.51
(−)-Chiragen 5,6-[p-xyl]	8.65	7.25	7.79	8.46	8.12	7.34	2.80	2.16	3.42	1.43	2.58	0.63	1.36

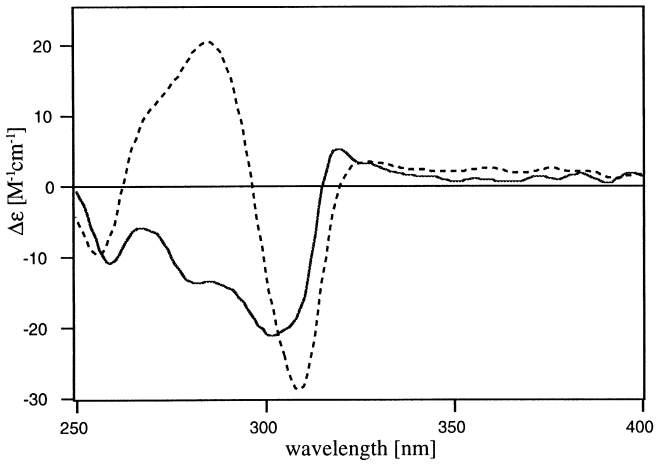


Figure 3. CD spectra of **L1** (dashed line) and **L2** (solid line) measured in dichloromethane.

(250 – 340 nm). Such CD signals are due to exciton coupling, often observed in coordinated bpy-type ligands.[15]

In the case of **L1** the spatial orientational average of the two bpy units relative to each other corresponds to a chiral configuration of the relatively close π systems, resulting in the exciton couplet with a minimum at 309 nm ($\Delta\varepsilon = -29\ M^{-1}cm^{-1}$) and a maximum at 285 ($\Delta\varepsilon = +20\ M^{-1}cm^{-1}$). The rotation about the C13–C13′ bond in **L2** is severely restricted. As a consequence, the CD spectrum of this ligand shows a reduced CD activity.

Metal complexes: Since the *R,R,S* isomer is formed in a much larger proportion, not all complexes were studied in detail with both diastereomers. However, a sufficient number of X-ray structures could be solved to allow a detailed discussion of the coordination behavior of these ligands.

All complexes that could be studied by NMR spectroscopy, with the exception of the paramagnetic Cu^{II} species, show the same number of protons as the free ligand. The protons of the bridgehead (H13) show the strongest shift, more significant for complexes with **L1** ($\Delta\delta = 0.7$ ppm) than those with **L2** ($\Delta\delta = 0.5$ ppm, see Figure 4 and the Experimental Section). In

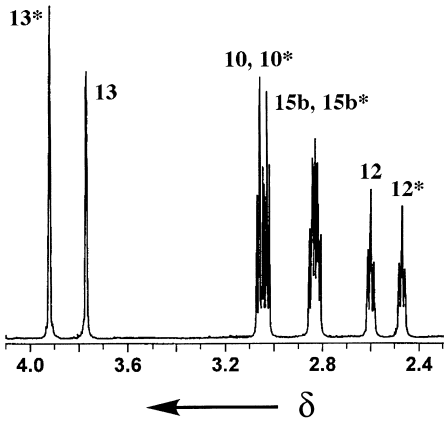


Figure 4. Fragment of the ^{1}H NMR spectrum (300 MHz, CD_3CN) of a mixture of two diastereoisomers [Pd**L1**]$(PF_6)_2$ and [Pd**L2**]$(PF_6)_2$ (with *).

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addition the spectra are well resolved. These observations clearly show that the ligand retains its C_2-symmetry in solution upon complexation. Furthermore, it indicates configurational stability of the complexes in solution.

Coordination number 4

Complexes of Ag^I with L1: With Ag^I, only the complex with the *R,R,S* isomer of the *Chiragen[0]* was obtained. It was fully characterized, including an X-ray structure analysis (Table 3).

The structure of the cation given in Figure 5 shows a coordination geometry that can be considered to be either a very strongly distorted (flattened) tetrahedron, or a helically twisted square. A somewhat similar structure was recently obtained by McCleverty et al.[16] with another tetradentate diimine type ligand. However, the *Chiragen* shows a predetermined chiral configuration, whereas the complex with the achiral diimine ligand yields a chiral but racemic coordination species.

The absolute configuration of $[Ag\mathbf{L1}]^+$ is Δ, as can be seen from Figure 5b. The angle between the two N-Ag-N chelate planes is 25.4°, rendering the structure closer to a planar, rather than a tetrahedral geometry. In agreement with the relatively large ionic radius of Ag^I, the metal to nitrogen distances (Table 4) are significantly bigger than the other complexes discussed below. The bite angles of the bpy units are consequently smaller than in the complexes with the smaller metal ions (Table 5). The exciton couplet in the CD spectrum (Figure 6) is in full agreement with the assignment of the configuration.

Complexes of Pd^{II} with L1 and L2: Although ligand **L2** is formed in a much smaller amount than **L1** (ca. 1:10) the only complex which can be crystallized from a mixture of $[Pd\mathbf{L1}]^{2+}$ and $[Pd\mathbf{L2}]^{2+}$ in acetonitrile by slow diffusion of diethyl ether is the complex $[Pd\mathbf{L2}](PF_6)_2$, because of its strongly reduced solubility. The two complexes have also

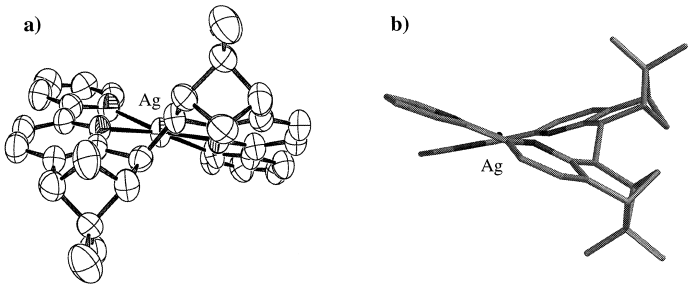

Figure 5. Representation of the cation $[Ag\mathbf{L1}]^+$: a) parallel (ORTEP) and b) perpendicular to the C_2 crystallographic axis. Hydrogen atoms are omitted for clarity.

Table 3. X-ray crystallographic data collection and refinement details for $[Ag\mathbf{L1}](PF_6)$, $[Pd\mathbf{L1}](PF_6)_2$, and $[Pd\mathbf{L2}](PF_6)_2$.

	$[Ag\mathbf{L1}](PF_6)$	$[Pd\mathbf{L1}](PF_6)_2$	$[Pd\mathbf{L2}](PF_6)_2$
formula	$C_{34}H_{34}N_4PF_6Ag(C_4H_{10}O)_{0.5}(H_2O)_{0.25}$	$C_{34}H_{34}N_4F_{12}P_2Pd$	$C_{34}H_{34}N_4F_{12}P_2Pd$
crystal appearance	pale yellow rods	yellow blocks	yellow rods
mol. weight	793.06	894.99	894.99
crystal system	orthorombic	orthorombic	trigonal
space group	$P2_12_12_1$	$P2_12_12_1$	$P3_1$
a [Å]	10.9300(8)	14.1480(10)	14.7064(9)
b [Å]	14.7695(11)	15.2271(11)	14.7064(9)
c [Å]	23.055(3)	16.843(13)	13.8813(10)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	90	90	120
volume [Å^3]	3721.7(6)	3486.6(5)	2600.0(3)
Z	4	4	3
ρ [g cm^{-1}]	1.415	1.705	1.715
μ [mm^{-1}]	0.647	0.721	0.726
crystal size [mm]	$0.6 \times 0.2 \times 0.1$	$0.4 \times 0.2 \times 0.2$	$0.2 \times 0.1 \times 0.1$
temperature [K]	223(2)	223(2)	223(2)
radiation [Å]	$Mo_{K\alpha}$ ($\lambda = 0.71073$)	$Mo_{K\alpha}$ ($\lambda = 0.71073$)	$Mo_{K\alpha}$ ($\lambda = 0.71073$)
scan type	ϕ oscillation	ϕ oscillation	ϕ oscillation
θ max [°]	$2.06 < \theta < 26.0$	$1.96 < \theta < 25.9$	$2.17 < \theta < 25.87$
measured reflections	29564	20475	20405
independent reflections	6938	6719	6652
reflections in refinement	2918, $I \geq 2\sigma(I)$	6196, $I \geq 2\sigma(I)$	4639, $I \geq 2\sigma(I)$
R[a]	0.0522	0.0280	0.0384
wR_2	0.1151	0.0718	0.0652
R[a] (all data)	0.1254	0.0318	0.0685
wR_2[b] (data)	0.1354	0.0737	0.0706
absolute structure param.	0.03(5)	−0.032(18)	−0.01(2)

[a] R_1 factor definition: $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] SHELXL-97 wR_2 factor definition: $wR_2 = [\Sigma w(F_o^2 - F_c^2)2/\Sigma w(F_o^4)]1/2$. Weighting scheme: $w = 1/[\sigma^2(F_o)^2 + (np)^2 + 0.00p]$, $p = (\max(F_o^2) + 2F_c^2)/3$.

Table 4. Metal-to-ligand bond lengths [Å] in the complexes.

	$[Ag\mathbf{L1}]^+$	$[Pd\mathbf{L1}]^+$	$[Pd\mathbf{L2}]^{2+}$	$[Zn\mathbf{L2}]^+$	$[Zn\mathbf{L1}(ClO_4)]^+$	$[Cu\mathbf{L1}Br]^+$	$[Zn_2\mathbf{L1}_2OH]^{3+}$	$[Zn\mathbf{L1}(NO_3)]^{+}$[a]
M–N1	2.298(7)	2.035(2)	2.018(4)	2.070(2)	2.076(2)	1.95(1)	2.088(5) 2.164(5)	2.107(6)
M–N2	2.347(7)	2.053(2)	2.026(4)	2.052(2)	2.065(2)	2.060(9)	2.124(5) 2.122(5)	2.101(5)
M–N1′	2.289(7)	2.016(3)	2.002(4)	2.054(2)	2.091(2)	2.05(1)	2.140(5) 2.091(5)	2.085(6)
M–N2′	2.359(7)	2.070(2)	2.067(4)	2.039(2)	2.066(2)	1.99(1)	2.120(5) 2.103(4)	2.094(5)
M–X	–	–	–	–	2.316(2) (X = O)	2.512(2) (X = Br)	2.011(4) 2.009(4) (X = O)	2.354(8) 2.421(8) (X = O)

[a] For the molecule with coordination number 6.

Table 5. Selected bite and dihedral angles (the angle between the two planes formed by the metal and two nitrogen atoms belonging to the same bipyridine unit) determined in the complexes.

	[Ag**L1**](PF$_6$)	[Pd**L1**](PF$_6$)$_2$	[Pd**L2**](PF$_6$)$_2$	[Zn**L2**](ClO$_4$)$_2$	[Zn**L1**(ClO$_4$)](ClO$_4$)	[Cu**L1**Br](PF$_6$)	[Zn$_2$**L1**$_2$(μ-OH)](ClO$_4$)$_3$
N1-M-N2	72.3(3)	80.69(10)	81.93(16)	81.56(9)	80.83(9)	81.7(5)	79.8(2) 76.1(2)
N1′-M-N2′	72.2(2)	80.67(10)	80.43(16)	81.36(9)	80.71(9)	80.9(4)	76.6(2) 81.30(19)
dihedral angle	25.4(4)	27.4(14)	− 28.3(2)	− 38.0(15)	33.1(14)	54.2(4)	49.8(3) 47.7(3)

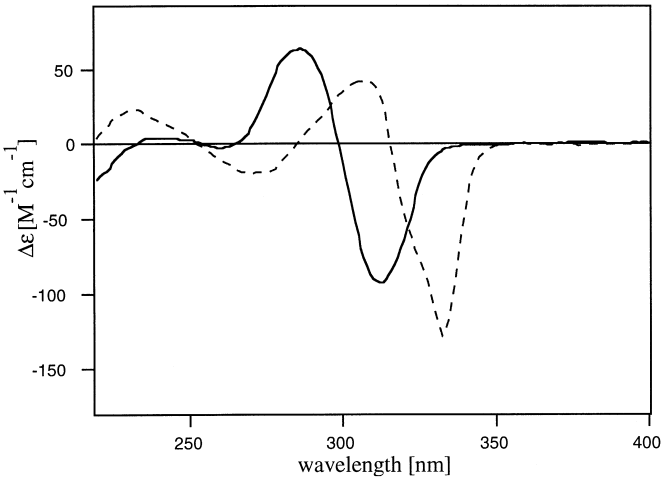

Figure 6. CD spectra of [Ag**L1**](PF$_6$) (solid line), and [Cu**L1**Br](PF$_6$) (dashed line).

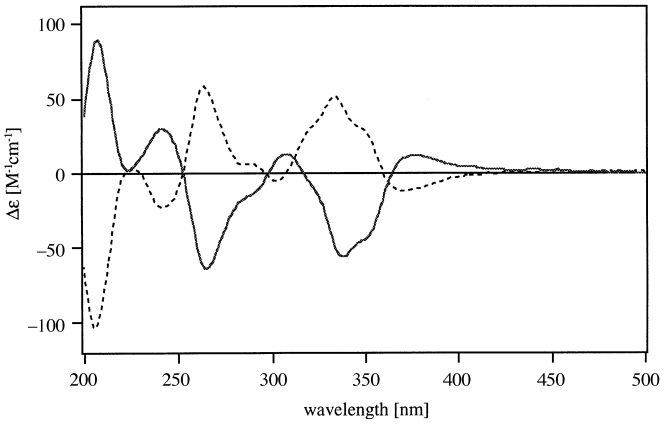

Figure 8. CD spectra of [Pd**L1**](PF$_6$)$_2$ (solid line) and [Pd**L2**](PF$_6$)$_2$ (dashed line).

been synthesized separately using diastereomerically pure ligands. It is more difficult to crystallize [Pd**L1**](PF$_6$)$_2$. In this case crystals for X-ray diffraction could be obtained by slow cooling of the solution of the complex in acetone/ethanol (from 50 °C to − 10 °C).

The cation of [Pd**L1**](PF$_6$)$_2$ has a structure similar to the Ag complex (Figure 7a). The absolute configuration is the same as in [Ag**L1**]$^+$. The most notable difference is the M–N distances of about 2.3 Å for the Ag complex and 2.01 Å for the Pd complex.

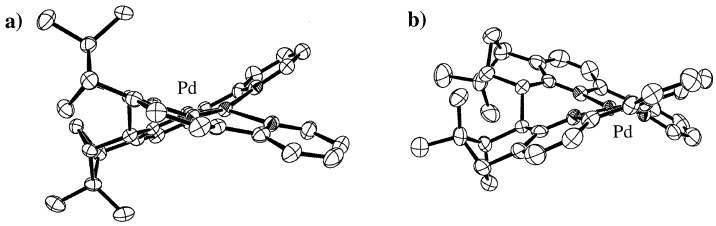

Figure 7. Perpendicular ORTEP views to the C_2 crystallographic axis of [Pd**L1**]$^+$ (a) and [Pd**L2**]$^+$ (b) ions. Hydrogen atoms are omitted for clarity.

The X-ray structure of [Pd**L2**](PF$_6$)$_2$ (Figure 7b) again shows a helically distorted square-planar coordination. However, the absolute configuration at the metal center is inverted as compared with complexes formed by **L1** (Δ for [Pd**L1**]$^{2+}$ and Λ for [Pd**L2**]$^{2+}$). This is corroborated by their respective CD spectra (Figure 8). The two spectra are not exact mirror images, since they result from diastereoisomers and not enantiomers.

It has to be stressed that these two configurations at the metal center have been obtained by using the same enantiomer of the α-pinene, (−)-α-pinene, as starting material in the ligand synthesis. The difference is due to the inverted configuration at the bridgeheads connecting the two halves of the *Chiragen* ligand.

In the complex with the *R,R,S*-configured *Chiragen* ligand the four methyl groups of the pinene point away from the "coordination plane", whereas they are forced into the "plane" in the *R,R,R*-configured form. The helical deviation from planarity is approximately the same for the two complexes (being slightly larger in the case of the *R,R,R* stereoisomer), but with opposite sign (see Table 5). This shows that the chirality at the metal center is mainly determined by the configuration of the carbon centers at the bridgehead positions. The angles between N–Pd–N planes are − 28.3° for (*R,R,R*) and 27.4° for (*R,R,S*).

Complexes with higher coordination numbers

Complexes of Zn^{II} with L1 and L2: The Zn^{II} cation is known for its chameleon-like behavior[17] and our findings confirm this designation. Three different solids were obtained by variation of the anion and/or the crystallization conditions (Table 6).

Using the mixture of **L1** and **L2** in the 10:1 ratio obtained after the oxidative coupling, crystalline {[Zn**L1**][Zn**L2**]}-(ClO$_4$)$_4$ is obtained by slow diffusion of diethyl ether into a solution of the complex in CH_3NO_2. The crystal lattice thus contains two independent complexes in a 1:1 ratio, one with **L1** and the other with the "inverted" ligand **L2**, despite the fact that **L1** is present in a 10-fold higher concentration in solution than **L2**. The structure of the [Zn**L2**]$^{2+}$ ion (Figure 9a) is very similar to that of [Pd**L2**]$^{2+}$ (Tables 3 and 4).

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Table 6. X-ray crystallographic data collection and refinement details for $[(Zn\mathbf{L1})_2OH](ClO_4)_3$, $[Cu\mathbf{L1}Br](PF_6)$, $[Zn\mathbf{L1}Zn\mathbf{L2}](ClO_4)_4$ and $[Zn\mathbf{L1}NO_3](NO_3)$ (for the molecule with coordination number 6).

	$[Cu\mathbf{L1}Br](PF_6)$	$[(Zn\mathbf{L1})_2OH](ClO_4)_3$	$[Zn\mathbf{L1}Zn\mathbf{L2}](ClO_4)_4$	$[Zn\mathbf{L1}NO_3](NO_3)$
formula	$CuBr(C_{34}H_{34}N_4)(PF_6)(CH_3CN)$	$[(C_{34}H_{34}N_4)Zn(OH)Zn(C_{34}H_{34}N_4)](ClO_4)_3(CH_3CN)_3(H_2O)$	$C_{34}H_{34}N_4Cl_2O_8Zn(CH_3NO_2)$	$C_{34}H_{34}N_4Zn(NO_3)_2(H_2O)_{1.21}(CH_3CN)_{0.29}(C_4H_{10}O)_{0.07}$
crystals appearance	green needles	colorless blocks	colorless rods	colorless rods
mol. weight	828.1	1580.55	823.97	725.66
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1$	$P2_1$	$P1$	$P2_1$
a [Å]	14.024(2)	14.1398(8)	7.0155(9)	24.9123(13)
b [Å]	7.1274(7)	15.8595(9)	15.137(2)	19.7696(15)
c [Å]	18.046(2)	16.2898(10)	16.909(2)	26.0354(13)
α [°]	90	90	89.233(15)	90
β [°]	101.248(5)	95.209(7)	78.773(15)	104.180(6)
γ [°]	90	90	84.444(15)	0
volume [Å^3]	1769.1(4)	3637.9(4)	1753.0(4)	12431.9(13)
Z	2	2	2	14
ρ [g cm^{-3}]	1.555	1.443	1.561	1.357
μ [mm^{-1}]	3.195	0.842	0.92	0.748
crystal size	$0.054 \times 0.1 \times 0.32$	$0.2 \times 0.1 \times 0.1$	$0.7 \times 0.25 \times 0.25$	$0.7 \times 0.25 \times 0.25$
temperature [K]	200(2)	223(2)	223(2)	223(2)
radiation [Å]	$Cu_{K\alpha}(\lambda = 1.5418)$	$Mo_{K\alpha}$ ($\lambda = 0.71073$)	$Mo_{K\alpha}(\lambda = 0.71073)$	$Mo_{K\alpha}(\lambda = 0.71073)$
Scan type	ω-2θ	ϕ oscillation	ϕ oscillation	ϕ oscillation
θ max [°]	$1 < \theta < 54$	$2.0 < \theta < 25.97$	$2.46 < \theta < 25.91$	$1.97 < \theta < 25.95$
measured reflections	4734	28838	13780	44303
independent reflections	4307	14077	11402	44303
reflections in refinement	3737, $\lvert F \rvert > 4\sigma$ (F_o)	5477, $I \geq 2\sigma(I)$	10578, $I \geq 2\sigma(I)$	22443, $I \geq 2\sigma(I)$
R[a]	0.055	0.0416	0.0291	0.0677
wR_2[b]	0.055[c]	0.0578	0.0711	0.1579
R[a] (all data)	–	0.1528	0.0323	0.1291
wR_2[b] (all data)	–	0.0805	0.0722	0.1823
absolute structure param.	0.00(0)	– 0.014(11)	– 0.013(6)	0.001(10)

[a] R_1 factor definition: $R = \Sigma(\lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert)/\Sigma\lvert F_o \rvert$. [b] SHELXL-97 wR_2 factor definition: $wR_2 = [\Sigma w(F_o^2 - F_c^2)2/\Sigma w(F_o^4)]1/2$. Weighting scheme: $w = 1/[\sigma^2(F_o)^2 + (np)^2 + 0.00p]$, $p = (\max(F_o^2) + 2F_c^2)/3$. [c] $w = 1/[\sigma 2(F_o) + 0.0002(F_o)^2]$.

probably due to favorable packing conditions. Using either pure **L1** or **L2** with $Zn(ClO_4)_2$ yields the quasimirror CD spectra shown in Figure 10. Again the sign of the exciton band at 330 nm is in agreement with the absolute configuration.

Recrystallization of the Zn^{II} complex described above from acetonitrile containing small amounts of water yields crystals of composition $[(Zn\mathbf{L1})_2OH](ClO_4)_3$. X-ray structure analysis reveals a hydroxy-bridged dimeric $[\mathbf{L1}Zn\text{-}(\mu\text{-}OH)\text{-}Zn\mathbf{L1}]^{3+}$ cation (Figure 11), where each metal center has trigonal-bipyramidal (TB-5) coordination geometry.

At each Zn center **L1** occupies two axial and two equatorial positions. The hydroxy ligand is located at the third equatorial position, forming the bridge between the two metals, which are crystallographically inequivalent but topographically the same. Each pair of axial ligand atoms at one center comes from one terminal pyridine and a pyridine adjacent to the pinene. The edge configuration (Figure 12) is inherently chiral.

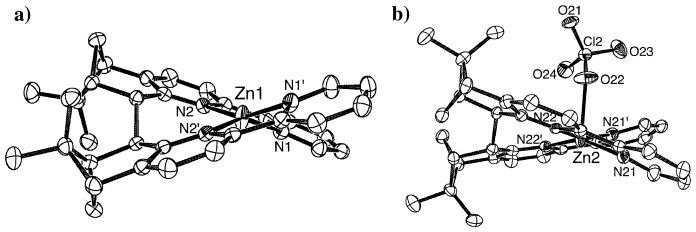


Figure 9. ORTEP representations of the cations $[Zn\mathbf{L2}]^{2+}$ (a) and $[Zn\mathbf{L1}ClO_4]^+$ (b) in the compound $[Zn\mathbf{L1}Zn\mathbf{L2}](ClO_4)_4$. Hydrogen atoms are omitted for clarity.

The second complex in the unit cell is a five-coordinate species (Figure 9b) with the more abundant **L1** ligand and one loosely bound ClO_4^- ion, with a Zn–O distance of 2.316 Å. The Cl-O-Zn angle of 130.7° is similar to that found in other coordinated perchlorates (136.2°).[18] One reason for the increased coordination number in $[Zn\mathbf{L1}ClO_4]^+$ as compared with $[Zn\mathbf{L2}]^{2+}$ is most likely the smaller dihedral angle of 33° between the N-Zn-N of the two bipyridine moieties (see Table 4). In $[Zn\mathbf{L2}]^{2+}$ the same angle amounts to 38°, making the metal somewhat less accessible for additional coordination. The 1:1 stoichiometry in the crystal lattice is most

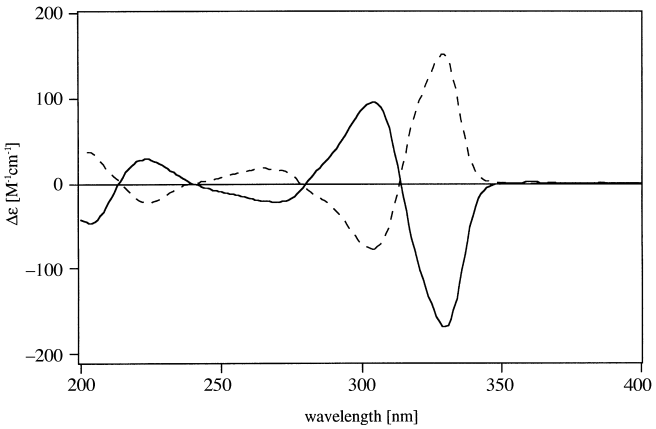


Figure 10. CD spectra of the complexes: $[Zn\mathbf{L1}ClO_4](ClO_4)$ (solid line) and $[Zn\mathbf{L2}](ClO_4)_2$ (dashed line).

The six chiral carbon atoms in *(–)-5,6-Chiragen[0]*, particularly the two centers at the bridgehead atoms C13 and C13′, render the two edge configurations diastereoisomeric. In fact, ligand **L1** yields, as in all other cases studied so far, only one of

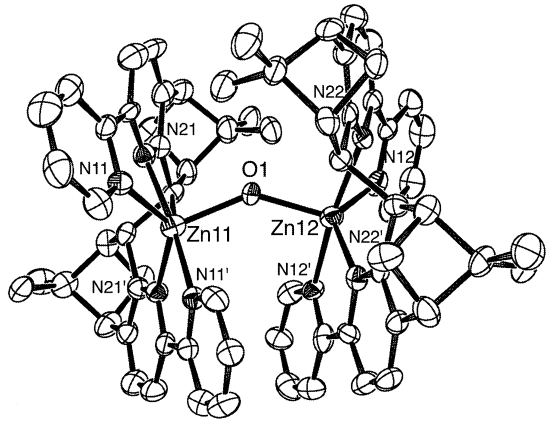
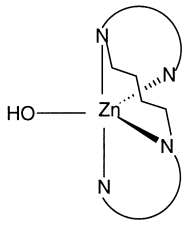


Figure 11. ORTEP representation of the cation $[(Zn\mathbf{L1})_2\mu\text{-OH}]^+$. Hydrogen atoms are omitted for clarity.



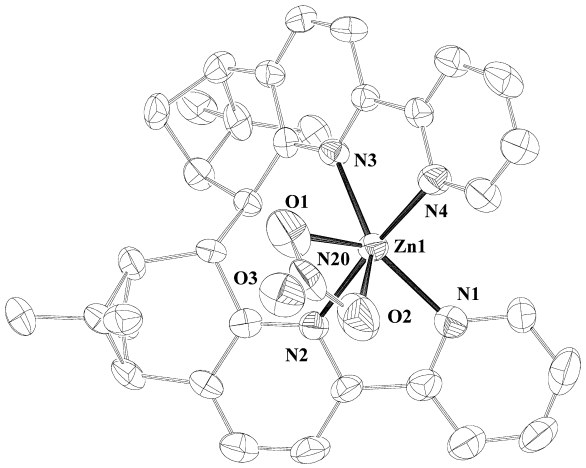
Δ

Figure 12. Chiral edge configurations Δ, as found in the dinuclear OH-bridged complex of $[(Zn\mathbf{L1})_2\mu\text{-OH}]^+$.

the two possible stereoisomers, leading to a homochiral *ΔΔ* dimer.

Using NO_3^- as anion and diastereoisomerically pure **L1**, $Zn\mathbf{L1}(NO_3)_2$ can be obtained quantitatively in crystalline form. The crystals are of space group $P2_1$ and have seven independent molecules per unit cell. In one of the molecules (Figure 13a), the NO_3^- acts as a bidentate ligand with two very similar Zn–O distances (2.35 and 2.42 Å), whereas in the other six complexes the nitrate ligand approaches the metal with one of the oxygen atoms (Figure 13b) significantly closer (2.10–2.20 Å) than the second (2.57–2.87 Å). These results indicate that there is a similar tendency toward both five and six coordination in the Zn coordination sphere. All complexes have Δ absolute configuration, with respect to the two bipyridine moieties of the *Chiragen* ligand. The CD spectra are in agreement with this assignment. The NMR spectra clearly show the C_2-symmetry of the complexes.

Copper complex with L1: Upon addition of $[Cu(CH_3CN)_4(PF_6)]$ to a solution containing **L1** at room temperature under argon atmosphere, the solution immediately turns deep blue. After the addition of an equimolar amount of NaBr, followed by precipitation with diethyl ether, a green compound $[Cu\mathbf{L1}Br](PF_6)$ is obtained. X-ray diffraction shows a mononuclear five-coordinate copper(II) in an environment that can be considered to be between a tetragonal pyramid (TPY-5) and a trigonal bipyramid (TB-5) (Figure 14). In the former the base of the pyramid is formed by the four nitrogen donors, and the bromine ligand occupies the apical position. However, this "chemical" way of looking at this structure is very approximate, since the four nitrogen donors are not coplanar. From a geometrical point of view, the structure is closer to a trigonal-bipyramid with N2, N4, and Br in equatorial, N3 and N1 in apical positions. With this assignment, the five-coordinate structure $[Cu\mathbf{L1}Br]^+$ and that found in $[\mathbf{L1}Zn\text{-}(\mu\text{-OH})\text{-}Zn\mathbf{L1}]^{3+}$ are closely related, both having a predetermined Δ configuration at the metal center. This is also confirmed by similar CD spectra. The facile oxidation to Cu^{II}, most probably by dissolved O_2, seems to be favored by the geometry of the ligand, since bis-complexes with unconnected pinene bipyridine ligands are very stable in the Cu^I oxidation state.



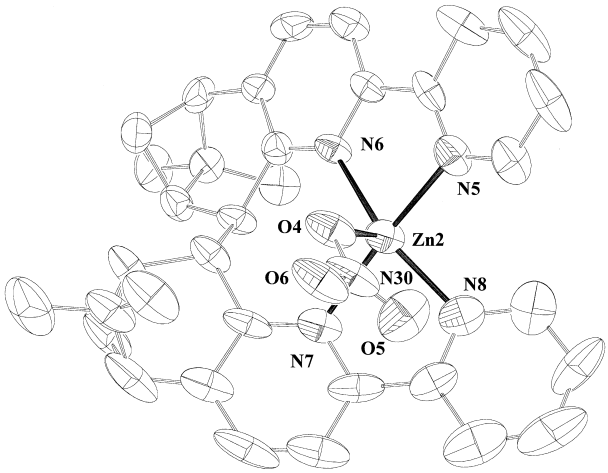


Figure 13. ORTEP representations of the cations $[Zn\mathbf{L1}NO_3]^+$ with coordination number 6 (top) and 5 (bottom). Hydrogen atoms are omitted for clarity.

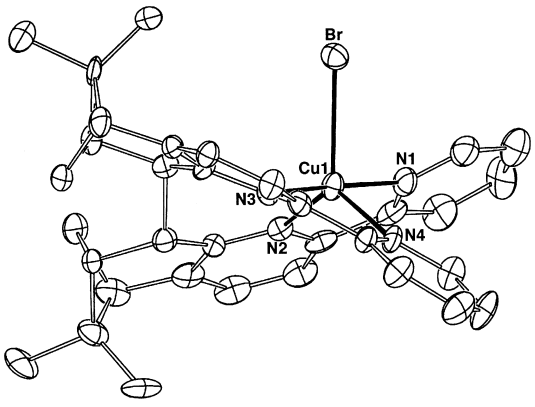


Figure 14. ORTEP representation of the cation $[Cu\mathbf{L1}Br]^+$. Hydrogen atoms are omitted for clarity.

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Cadmium complex with L1: No high quality X-ray data were obtained for the compound $[(H_2O)Cd\mathbf{L1}(\mu\text{-}ClO_4)Cd\mathbf{L1}(ClO_4)][Cd_2\mathbf{L1}_2(ClO_4)_2(\mu\text{-}ClO_4)](ClO_4)_3$, due to the twinning of the crystals. The final *R* value of 0.13 does not allow for a detailed analysis of the structure. However, some features (Figures 15a and 15b) can be discussed. The Cd centers are all octahedrally coordinated, with ligand **L1** occupying a distorted equatorial plane of the octahedron. The remaining *trans* positions of the octahedra are occupied by coordinated ClO_4^- or in one case by a water molecule.

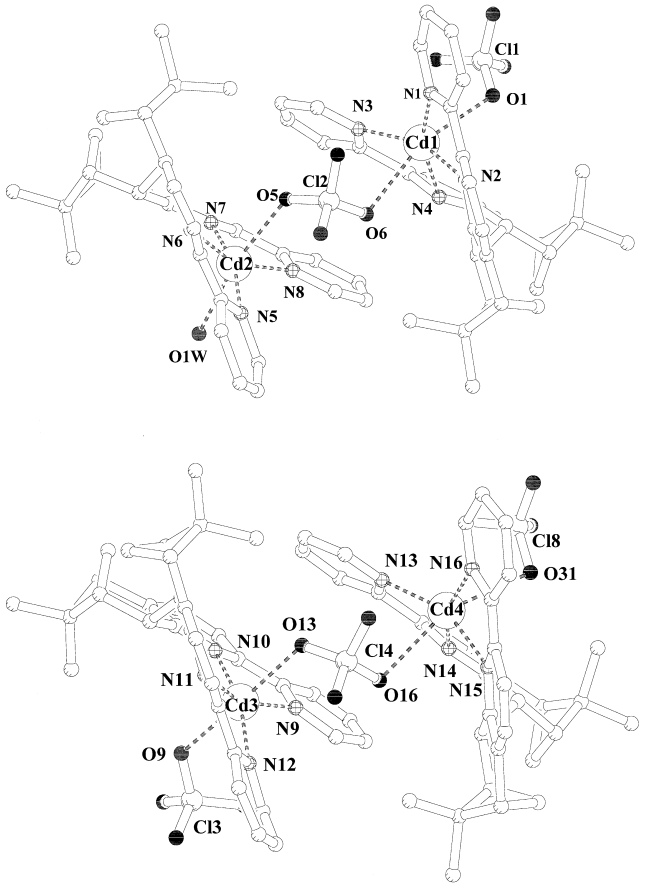

Figure 15. Ball and stick representations of the cations $[(H_2O)Cd\mathbf{L1}(\mu\text{-}ClO_4)Cd\mathbf{L1}(ClO_4)]^{2+}$ (top) and $[Cd_2\mathbf{L1}_2(ClO_4)_2(\mu\text{-}ClO_4)]^+$ (bottom), without hydrogens.

This *trans* configuration corresponds to an inherently achiral arrangement,[19] (see also Figure 1) of a topologically linear tetradentate ligand. However, the chiral ligand decreases the idealized symmetry of this configuration from C_{2v} to C_2. As expected, and in analogy with the structure of the Ag^I and Pd^{II} complexes, the two halves of the ligand define two skew lines of the Δ configuration. There are two dinuclear species in the unit cell, in each of them ClO_4^- bridges the two Cd centers.

Conclusion

The two newly introduced ligands *(−)-5,6-Chiragen[0] (R,R,S)* **L1** and *(−)-5,6-Chiragen (R,R,R)* **L2**, both derived from the same chiral pool precursor, *(−)-α*-pinene, go a long way in our aim to predetermine the chirality at metal centers. With these tetradentate ligands it is now possible to synthesize metal complexes with coordination numbers four, five, and six having different coordination geometries, with complete control of their stereochemical configuration. The two ligands yield species of opposite chirality at the metal centers. These *Chiragen* type ligands are two representatives of a class of molecules that may be engineered for total control of the stereochemistry of coordination species.

Experimental Section

General: Caution: perchlorate salts are potentially explosive! All commercial chemicals (Fluka, Merck, or Strem Chemicals) were of best available grade and used without further purification. The ligand (−)-5,6-pinene bipyridine was prepared according to published procedures.[20] NMR spectra (^1H, ^{13}C, 2D-COSY, $^1H^{13}C$-HETCOR, and decoupling experiments) were recorded either on a Varian Gemini 300 or Bruker Avance DRX500 instrument, with residual solvent peak as standard. Chemical shifts are reported in ppm on the δ scale. Mass spectral data were obtained on a Bruker FTMS 4.7 T BioApex II using a standard electrospray ion source and a VG Instruments 7070E with a FAB inlet system. Electronic spectra were measured using a Perkin Elmer Lambda 40. The results are given in λ[nm] versus ε [$M^{-1}cm^{-1}$]. CD spectra were recorded on a Jasco J-715 spectropolarimeter and the results are given in [nm] versus $\Delta\varepsilon$ [$M^{-}cm^{-1}$]. Rotation angles were obtained with a Perkin Elmer MC-241 polarimeter.

The numbering scheme of the ligands is given in Figure 2.

Ligand L1: Dry THF (10 mL) was cooled to −20 °C in a two-necked flask equipped with a septum and connected to an argon line. Under stirring, diisopropylamine (0.46 mL, 3 mmol) and BuLi (1.87 mL 1.6 M in hexane, 3 mmol) were injected. The temperature was raised to 0 °C (water-ice bath) for 10 min and then dropped to −40 °C. The (−)-5,6-pinene–bpy (504 mg, 2 mmol), dissolved in dry THF (10 mL), was added dropwise over 30 min. The dark solution was stirred at −40 °C for 4 h, then I_2 (254 mg, 1 mmol) dissolved in THF (10 mL) was injected slowly over 30 min. The solution became orange and was stirred at room temperature overnight. Water (2 mL) was added in order to quench the reaction and the solution was concentrated to half of the volume under reduced pressure. After addition of a saturated aqueous solution of $NaHCO_3$ (30 mL), the mixture was extracted with CH_2Cl_2 (4 × 20 mL). The organic phase was dried ($MgSO_4$) and evaporated in vacuo. The brown residue was purified by silica gel column chromatography (72 %). R_f = 0.34 (hexane:EtOAc:TEA = 3:1:0.1) (TEA is triethylamine); Rotation angle (CH_2Cl_2, 25[a]°C): $[\alpha]_D$ = −65.5° mL g^{-1} dm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.61 (ddd, $^3J_{1,2}$ = 4.8 Hz, $^4J_{1,3}$ = 1.8 Hz, $^5J_{1,4}$ = 0.8 Hz, 2H; H(1)), 8.33 (d, $^3J_{4,3}$ = 7.8 Hz, 2H; H(4)), 8.10 (d, $^3J_{7,8}$ = 7.8 Hz, 2H; H(7)), 7.71 (ddd, $^3J_{3,4}$ = 7.8 Hz, $^3J_{3,2}$ = 6.0 Hz, $^4J_{3,1}$ = 1.8 Hz, 2H; H(3)), 7.34 (d, $^3J_{8,7}$ = 7.8 Hz, 2H; H(8)), 7.21 (ddd, $^3J_{2,1}$ = 4.8 Hz, $^3J_{2,3}$ = 6.0 Hz, $^4J_{2,4}$ = 1.2 Hz, 2H; H(2)), 4.58 (br s, 2H; H(13)), 2.78 (dd, $^3J_{10,15b}$ = 5.7 Hz, $^4J_{10,12}$ = 5.7 Hz, 2H; H(10)), 2.49 (ddd, $^3J_{15b,10}$ = 5.7 Hz, $^3J_{15b,12}$ = 5.7 Hz, $^2J_{15b,15a}$ = 9.6 Hz, 2H; H(15b)), 2.13 (dd, $^3J_{12,15b}$ = 5.7 Hz, $^4J_{12,10}$ = 5.7 Hz, 2H; H(12)), 1.38 (d, $^2J_{15a,15b}$ = 9.6 Hz, 2H; H(15a)), 1.30 (s, 6H; H(17)), 0.76 (s, 6H; H(16)); ^{13}C NMR (75.44 MHz, $CDCl_3$, 25 °C): δ = 158.27 (q), 157.00 (q), 152.93 (q), 148.84 (C(1)), 143.12 (q), 138.65 (q), 136.75 (C(3)), 133.51 (C(8)), 123.00 (C(2)), 120.81 (C(4)), 117.67 (C(7)), 46.42 (C(10)), 46.25 (C(13)), 42.74 (C(12)), 41.87 (q, C(11)), 29.07 (C(15)), 26.33 (C(17)), 21.03 (C(16)); CD (CH_3CN, 3.95 × 10^{-5} M): λ ($\Delta\varepsilon$) = 256 (−10), 284 (+20), 309 (−29); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 251 (1.8 × 10^4, sh), 256 (1.85 × 10^4), 297 (3.5 × 10^4), 308 (2.6 × 10^4, sh); MS (FAB, m-nitrobenzyl alcohol): *m/z* (%): 499 (100) [**L1**]$^+$, 249 (30) [**L1** − $C_{17}H_{17}N_2$]$^+$; elemental analysis (%) calcd for $C_{34}H_{34}N_4$: C 81.89, H 6.87, N 11.24; found: C 81.62, H 7.03, N 11.04.

Ligand L2: The ligand was obtained as a by-product in the coupling reaction used to produce the ligand *(−)-Chirogen [0] S,S* (ratio 1:10). After purification by column chromatography, the fraction collected (R_f = 0.23) contained the other diastereoisomer also. For complete separation a Lobar (Merck) column (silica gel 40–63 μm) was used (hexane:CH_2Cl_2:TEA =

4:1:0.1. $R_f = 0.18$) yielding 6%. Rotation angle (CH_2Cl_2, 22°C): $[\alpha]_D = -268^\circ$ mL g^{-1} dm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): $\delta = 8.27$ (ddd, $^3J_{1,2} = 4.7$ Hz, $^4J_{1,3} = 1.8$ Hz, $^5J_{1,4} = 0.9$ Hz, 2H; H(1)), 7.88 (d, $^3J_{7,8} = 7.8$ Hz, 2H; H(7)), 7.37 (d, $^3J_{8,7} = 7.8$ Hz, 2H; H(8)), 7.30 (ddd, $^3J_{3,2} = 7.4$ Hz, $^3J_{3,4} = 7.6$ Hz, $^4J_{3,1} = 1.8$ Hz, 2H; H(3)), 7.09 (d, $^3J_{4,3} = 7.6$ Hz), 2H; H(4)), 6.94 (ddd, $^3J_{2,1} = 4.7$ Hz, $^3J_{2,3} = 7.4$ Hz, $^4J_{2,4} = 1.2$ Hz, 2H; H(2)), 3.6 (s, 2H; H(13)), 2.84 (2H; H(10), superposition with H(15b)), 2.79 (2H; H(15b), superposition with H(10)), 2.65 (dd, $^3J_{12,15b} = 6.12$ Hz, $^4J_{12,10} = 6.1$ Hz, 2H; H(12)), 1.51 (s, 6H; H(17)), 1.36 (s, 6H; H(16)), 1.33 (H(15a) partially superposed with H(16)); ^{13}C NMR (75.44 MHz, $CDCl_3$, 25°C): $\delta = 157.3$ (q), 156.1 (q), 151.8 (q), 148.2 (C(1)), 142.3 (q), 136.1 (C(3)), 133.0 (C(8 or 7)), 122.5 (C(2)), 120.4 (C(4)), 116.8 (C(7 or 8)), 50.7 (C(13)), 47.8 (C(10)), 45.2 (C(12)), 39.7 (q, C(11)), 34.4 (C(15)), 27.6 (C(17)), 23.3 (C(16)); CD (CH_2Cl_2, 1.11×10^{-4} M, 0.1 cm cell): λ ($\Delta\varepsilon$) = 319 (5), 302 (−21), 286 (sh, 14), 268 (−6), 259 (−11); UV/Vis (CH_2Cl_2, 1.11×10^{-4} M, 0.1 cm cell): λ_{max} (ε) = 308 (22×10^3, sh), 296 (29×10^3), 254 (18×10^3); HRMS (ESI): calcd for [**L2**]$^+$ 499.28562, found 499.28558.

[AgL1]PF$_6$: $AgPF_6$ (25.2 mg, 0.1 mmol) was dissolved in acetonitrile (3 mL) and the ligand **L1** (50 mg, 0.1 mmol) in acetonitrile/chloroform (2 mL: 2 mL) was added rapidly. The light yellow solution was stirred in the absence of light and after a few minutes about 5 mL of the solvent was removed under reduced pressure. The white complex was precipitated with *tert*-butyl methyl ether and filtered through a glass frit. The residue was dissolved in acetonitrile and the solution evaporated to dryness (96%). ^{1}H NMR (300 MHz, CD_3CN, 25°C): $\delta = 8.76$ (ddd, $^3J_{1,2} = 4.6$ Hz, $^4J_{1,3} = 1.7$ Hz, $^5J_{1,4} = 0.8$ Hz, 2H; H(1)), 8.19 (ddd, $^3J_{4,3} = 7.5$ Hz, $^4J_{4,2} = 1.1$, $^5J_{4,1} = 0.8$ Hz, 2H; H(4)), 7.93 (d, $^3J_{7,8} = 7.8$ Hz, 2H; H(7)), 8.06 (ddd, $^3J_{3,4} = 9.2$ Hz, $^3J_{3,2} = 7.6$ Hz, $^4J_{3,1} = 1.7$ Hz, 2H; H(3)), 7.58 (d, $^3J_{8,7} = 7.8$ Hz 2H; H(8)), 7.57 (ddd, $^3J_{2,1} = 4.6$ Hz, $^3J_{2,3} = 7.6$ Hz, $^4J_{2,4} = 1.1$ Hz, 2H; H(2)), 3.98 (s, 2H; H(13)), 2.94 (dd, $^3J_{10,15b} = 5.6$ Hz, $^4J_{10,12} = 5.6$ Hz, 2H; H(10)), 2.81 (ddd, $^3J_{15b,10} = 5.6$ Hz, $^3J_{15b,12} = 5.6$ Hz, $^2J_{15b,15a} = 9.7$ Hz, 2H; H(15b)), 2.61 (dd, $^3J_{12,15b} = 5.6$ Hz, $^4J_{12,10} = 5.6$ Hz, 2H; H(12)), 1.47 (d, $^2J_{15a,15b} = 9.7$ Hz, 2H; H(15a)), 1.35 (s, 6H; H(17)), 0.56 (s, 6H; H(16)); ^{13}C NMR (75.44 MHz, CD_3CN, 25°C): $\delta = 162.4$ (q), 154.3 (q), 152.4 (C(1)), 151.9 (q), 146.3 (q), 140.5 (C(3)), 136.2 (C(8)), 126.0 (C(2)), 123.8 (C(4)), 121.2 (C(7)), 48.8 (C(13)), 46.9 (C(10)), 42.8 (q, C(11)), 42.4(C(12)), 32.3 (C(15)), 26.7 (C(17)), 21.5 (C(16)); CD (CH_3CN, $1.86 \times 10 - ^4$ M, 0.1 cm cell): λ ($\Delta\varepsilon$) = 313 (−92), 287 (63); UV/Vis (CH_3CN, 1.86×10^{-4} M, 0.1 cm cell): λ_{max} (ε) = 297 (2.5×10^4), 273 (sh, 1.7×10^4), 264 (sh, 1.75×10^4), 258 (1.8×10^4); MS (FAB, *m*-nitrobenzyl alcohol): *m/z* (%): 605 (100) [$M - PF_6$]$^+$; elemental analysis (%) calcd for $AgC_{34}H_{34}N_4PF_6$: C 54.34, H 4.56, N 7.46; found: C 54.16, H 4.54, N 7.31.

[PdL1](PF$_6$)$_2$: To a solution of the ligand **L1** (50 mg, 0.1 mmol) in chloroform/methanol (1:20, 21 mL) was added solid $Pd(OCOCH_3)_2$ (22.4 mg). The suspension was stirred overnight at room temperature. The solvent was removed under high vacuum and the solid residue was redissolved in a minimum amount of methanol, filtered, and precipitated by addition of a methanolic solution of NH_4PF_6 5%. The precipitate was washed with methanol and dried (56%). ^{1}H NMR (500 MHz, CD_3CN, 25°C): $\delta = 8.36$ (4H; H(1), H(3)), 8.26 (ddd, $^3J_{4,3} = 8.25$ Hz, $^4J_{4,2} = 1.4$ Hz, $^5J_{4,1} = 0.5$ Hz, 2H; H(4)), 8.13 (d, $^3J_{7,8} = 8.0$ Hz, 2H; H(7)), 7.93 (d, $^3J_{8,7} = 8.0$ Hz, 2H; H(8)), 7.78 (ddd, $^3J_{2,1} = 5.9$ Hz, $^3J_{2,3} = 7.5$ Hz, $^4J_{2,4} = 1.4$ Hz, 2H; H(2)), 3.77 (s, 2H; H(13)), 3.03 (dd, $^3J_{10,15b} = 5.6$ Hz, $^4J_{10,12} = 5.6$ Hz, 2H; H(10)), 2.82 (ddd, $^3J_{15b,10} = 5.6$ Hz, $^3J_{15b,12} = 5.6$ Hz, $^2J_{15b,15a} = 10.3$ Hz, 2H; H(15b)), 2.47 (dd, $^3J_{12,15b} = 5.6$ Hz, $^4J_{12,10} = 5.6$ Hz, 2H; H(12)), 1.35 (d, $^2J_{15a,15b} = 10.3$ Hz, 2H; H(15a)), 1.4 (s, 6H; H(17)), 0.76 (s, 6H; H(16)); ^{13}C NMR (125.76 MHz, CD_3CN, 25°C): $\delta = 166.8$ (q), 159.0 (q), 156.0 (q), 152.3 (C(1)), 149.4 (q), 143.6 (C(3)), 139.4 (C(8)), 129.0 (C(2)), 124.8 (C(4)), 123.4 (C(7)), 48.1 (C(10)), 45.7 (C(13)), 41.5 (q, C(11)), 41.3 (C(12)), 31.2 (C(15)), 25.0 (C(17)), 20.9 (C(16)); CD (CH_3CN, 1.8×10^{-4} M, 0.1 cm cell): λ ($\Delta\varepsilon$) = 374 (11), 338 (−56), 308 (12), 26 (−64), 242 (30); UV/Vis (CH_3CN, 1.8×10^{-4} M, 0.1 cm cell): λ_{max} (ε) = 329 (24.1×10^3), 261 (32×10^3); MS (ES): *m/z* (%): 302.1 (60) [$M - 2PF_6$]$^{2+}$, 749.17 (100) [$M - PF_6$]$^+$; elemental analysis (%) calcd for $PdC_{34}H_{34}N_4P_2F_{12}$: C 45.63, H 3.83, N 6.26; found: C 46.0, H 3.99, N 6.21.

[PdL2](PF$_6$)$_2$: The complex was obtained following the same procedure as for the complex [Pd**L1**]$(PF_6)_2$ (50%). ^{1}H NMR (500 MHz, CD_3CN, 25°C): $\delta = 8.37$ (4H; H(1), H(3)), 8.26 (ddd, $^3J_{4,3} = 8.25$ Hz, $^4J_{4,2} = 1.4$ Hz, $^5J_{4,1} = 0.5$ Hz, 2H; H(4)), 8.14 (d, $^3J_{7,8} = 8.0$ Hz, 2H; H(7)), 7.95 (d, $^3J_{8,7} = 8.0$ Hz, 2H; H(8)), 7.79 (ddd, $^3J_{2,1} = 5.9$ Hz, $^3J_{2,3} = 7.5$ Hz, $^4J_{2,4} = 1.4$ Hz, 2H; H(2)), 3.92 (s, 2H; H(13)), 3.06 (dd, $^3J_{10,15b} = 5.6$ Hz, $^4J_{10,12} = 5.6$ Hz, 2H; H(10)), 2.83 (ddd, $^3J_{15b,10} = 5.6$ Hz, $^3J_{15b,12} = 5.6$ Hz, $^2J_{15b,15a} = 10.3$ Hz, 2H; H(15b)), 2.6 (dd, $^3J_{12,15b} = 5.6$ Hz, $^4J_{12,10} = 5.6$ Hz, 2H; H(12)), 1.51 (d, $^2J_{15a,15b} = 10.3$ Hz, 2H; H(15a)), 1.49 (s, 6H; H(17)), 0.67 (s, 6H; H(16)); ^{13}C NMR (75.44 MHz, CD_3CN, 25°C): $\delta = 166.7$ (q), 158.9 (q), 156.1 (q), 152.0 (C(1)), 149.3 (q), 143.6 (C(3)), 139.4 (C(8)), 129.0 (C(2)), 124.8 (C(4)), 123.5 (C(7)), 48.5 (C(13)), 46.9 (C(10)), 45.1 (C(12)), 38.8 (q, C(11)), 32.8 (C(15)), 25.6 (C(17)), 25.1 (C(16)); CD (CH_3CN, 2×10^{-4} M, 0.1 cm cell: λ ($\Delta\varepsilon$) = 371 (−13), 0347 (sh, 30), 335 (50), 303 (−6), 290 (sh, 6), 264 (58), 242 (−23), 227 (2), 206 (−104); UV/Vis (CH_3CN, 2×10^{-4} M, 0.1 cm cell,): λ_{max} (ε) = 390–461 (br., 457), 329 (24.7×10^3), 261 (32.5×10^3); HRMS (ESI): calcd for [$M - 2PF_6$]$^{2+}$ ($C_{34}H_{34}N_4{}^{106}Pd$) 302.09036, found 302.09053; calcd for [$M - PF_6$]$^+$ ($C_{34}H_{34}N_4P_6F^{106}Pd$) 749.14545, found 749.14581.

[ZnL1](ClO$_4$)$_2$: The ligand **L1** (50 mg, 0.1 mmol) was dissolved in $CHCl_3$ (10 mL) and CH_3CN (5 mL). To this solution was added $Zn(ClO_4)_2 \cdot 6H_2O$ (37 mg, 0.1 mmol) dissolved in CH_3CN (5 mL). After stirring, the solution was concentrated and diethyl ether was added dropwise. The white precipitate obtained was filtered off, washed with diethyl ether and dried (98%). ^{1}H NMR (300 MHz, CD_3CN, 25°C): $\delta = 8.62$ (dd, $^3J_{1,2} = 5.5$ Hz, $^4J_{1,3} = 1.71$ Hz, 2H; H(1)), 8.49 (d, $^3J_{4,3} = 8.1$ Hz, 2H; H(4)), 8.37 (d, $^3J_{7,8} = 8.0$ Hz, 2H; H(7)), 8.35 (ddd, $^3J_{3,4} = 8.1$ Hz, $^3J_{3,2} = 7.6$ Hz, $^4J_{3,1} = 1.71$ Hz, 2H; H(3)), 7.87 (d, $^3J_{8,7} = 8.0$ Hz, 2H; H(8)), 7.82 (ddd, $^3J_{2,1} = 5.5$ Hz, $^3J_{2,3} = 7.6$ Hz, $^4J_{2,4} = 1.07$ Hz, 2H; H(2)), 3.83 (s, 2H; H(13)), 3.10 (dd, $^3J_{10,15b} = 5.5$ Hz, $^4J_{10,12} = 5.5$ Hz, 2H; H(10)), 2.88 (ddd, $^3J_{15b,10} = 5.5$ Hz, $^3J_{15b,12} = 5.5$ Hz, $^2J_{15b,15a} = 10.01$ Hz, 2H; H(15b)), 2.54 (dd, $^3J_{12,15b} = 5.5$ Hz, $^4J_{12,10} = 5.5$ Hz, 2H; H(12)), 1.53 (d, $^2J_{15a,15b} = 10.01$ Hz, 2H; H(15a)), 1.43 (s, 6H; H(17)), 0.63 (s, 6H; H(16)); ^{13}C NMR (75.44 MHz, CD_3CN, 25°C): $\delta = 163.2$ (q), 151.1 (q), 149.1 (C(1)), 148.8 (q), 148.5 (q), 142.9 (C(3)), 139.1 (C(8)), 127.4 (C(2)), 123.4 (C(4)), 121.0 (C(7)), 47.7 (C(13)), 46.5 (C(10)), 42.4 (C(12)), 42.0 (q, C(11)), 31.9 (C(15)), 26.3 (C(17)), 21.0 (C(16)); CD (CH_3CN, 2.2×10^{-4} M, 0.1 cm cell): λ ($\Delta\varepsilon$) = 330 (−173), 305 (97), 270 (−22), 222 (29); UV/Vis (CH_3CN, 2.2×10^{-4} M, 0.1 cm cell,): λ_{max} (ε) = 327 (sh) (23×10^3), 312 (36×10^3), 273 (sh, 17×10^3), 264 (20.5×10^3); MS (FAB, *m*-nitrobenzyl alcohol): *m/z* (%): 661 (100) [$M - ClO_4$]$^+$, 562 (22) [$M - 2ClO_4$]$^{2+}$; MS (ES): *m/z*: 281 [$M - 2ClO_4$]$^{2+}$, 661 [$M - ClO_4$]$^+$; elemental analysis (%) calcd for $ZnC_{34}H_{34}N_4Cl_2O_8 + 0.5H_2O$: calcd C 52.9, H 4.57, N 7.26; found: C 52.77, H 4.53, N 6.96.

[ZnL2](ClO$_4$)$_2$: The complex was obtained following the same procedure as in the case of [Zn**L2**]$(ClO_4)_2$ but using ten times less of the compounds. ^{1}H NMR (500 MHz, CD_3CN, 25°C): $\delta = 8.5–8.46$ (4H; H(1), H(4)), 8.35 (ddd, $^4J_{3,1} = 1.7$ Hz, $^3J_{3,2} = 7.6$ Hz, $^3J_{3,4} = 9.2$ Hz, 2H; H(3)), 8.33 (d, $^3J_{7,8} = 8.0$ Hz), 7.94 (d, 2H; H(8), $^3J_{8,7} = 8.0$ Hz, 2H; H(7)), 7.77 (ddd, $^3J_{2,1} = 5.2$ Hz, $^3J_{2,3} = 7.6$ Hz, $^4J_{2,4} = 1.1$ Hz, 2H; H(2)), 4.03 (s, 2H; H(13)), 3.05 (dd, $^3J_{10,15b} = 8.0$ Hz, $^4J_{10,12} = 8.0$ Hz, 2H; H(10)), 2.86 (ddd, $^3J_{15b,10} = 5.8$ Hz, $^3J_{15b,12} = 5.8$ Hz, $^2J_{15b,15a} = 10.2$ Hz, 2H; H(15b)), 2.68 (dd, $^3J_{12,15b} = 5.8$ Hz, $^4J_{12,10} = 5.8$ Hz, 2H; H(12)), 1.53 (s, 6H; H(17)), 1.44 (d, $^2J_{15a,15b} = 10.2$ Hz, 2H; H(15a)), 0.71 (s, 6H; H(16)); ^{13}C NMR (75.44 MHz, CD_3CN, 25°C): $\delta = 162.7$ (q), 151.0 (q), 149.3 (C(1)), 149.0 (q), 148.3 (q), 143.4 (C(3)), 139.5 (C(8)), 127.7 (C(2)), 123.7 (C(4)), 121.8 (C(7)), 51.3 (C(13)), 47.7 (C(10)), 45.9 (C(12)), 39.3 (q, C(11)), 34.1 (C(15)), 25.9 (C(17)), 25.2 (C(16)); CD (CH_3CN, 1.5×10^{-4} M, 0.1 cm cell): λ ($\Delta\varepsilon$) = 330 (153), 304 (−78), 266 (18), 224 (−23); UV/Vis (CH_3CN, 1.5×10^{-4} M, 0.1 cm cell,): λ_{max} (ε) = 362 (sh, 14.1×10^3), 331 (38.7×10^3), 264 (sh, 46×10^3), 245 (52.4×10^3); HRMS (ESI): calcd for $C_{34}H_{34}N_4{}^{64}Zn$ [$M - 2ClO_4$]$^{2+}$ 281.10319, found 281.10315; calcd for $C_{34}H_{34}N_4{}^{64}Zn^{35}ClO_4$ [$M - ClO_4$]$^+$ 661.15545, found 661.15608.

[CuL1Br](PF$_6$): $[Cu(CH_3CN)_4](PF_6)$ (37.2 mg, 0.1 mmol) was added to a suspension of **L1** (50 mg, 0.1 mmol) in ethanol (15 mL). The solution immediately turned dark blue. After the mixture had been stirred for 1 h, the ligand was completely dissolved and NaBr (10.7 mg, 0.1 mmol) was added. After one night of stirring, part of the solvent was evaporated under low pressure and the remaining blue solution was filtered and precipitated by adding diethyl ether. The precipitate was washed with ethanol and diethyl ether and dissolved in chloroform. The color of the solution became green after a few minutes. This solution was evaporated to dryness and the resulting solid was analyzed (64%). CD (CH_3CN, 2.3×10^{-4} M, 0.1 cm cell): λ ($\Delta\varepsilon$) = 333 (−128), 307 (+41), 271 (−20), 233 (+23), 210 (−20); UV/Vis (CH_3CN, 2.3×10^{-4} M, 0.1 cm cell): λ_{max} (ε) = 380–450 (700), 328 (sh, 20×10^3), 315 (27.9×10^3), 258 (26×10^3); MS (ES): *m/z* (%): 642.1 (100) [Cu**L1**Br]$^+$, 280.6 (60) [Cu**L1**]$^{2+}$; elemental analysis (%) calcd for $CuC_{34}H_{34}N_4BrPF_6 + 2.5H_2O$: C 49.08, H 4.72, N 6.73; found: C 49.39, H 4.71, N 6.46.

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[ZnL1](NO$_3$)$_2$: $Zn(NO_3)_2\cdot 4H_2O$ (26 mg, 0.1 mmol) was dissolved in acetonitrile (10 mL). The ligand **L1** (50 mg, 0.1 mmol) dissolved in $CHCl_3$ (5 mL) was rapidly added to the clear solution. The mixture was stirred at room temperature overnight and the solvent removed. No further purification was necessary. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): $\delta = 8.47$ (2H; H(1), H(4), superposed), 8.31 (d, $^3J_{7,8} = 8$ Hz, 2H; H(7)), 8.30 (2H; H(3) superposed with H(7)), 7.86 (d, $^3J_{8,7} = 8$ Hz, 2H; H(8)), 7.72 (ddd, $^3J_{2,1} = 4.0$ Hz, $^3J_{2,3} = 7.5$ Hz, $^4J_{2,4} = 1.1$ Hz, 2H; H(2)), 3.90 (s, 2H; H(13)), 3.05 (dd, $^3J_{10,15b} = 5.8$ Hz, $^4J_{10,12} = 5.8$ Hz, 2H; H(10)), 2.85 (ddd, $^3J_{15b,10} = 5.8$ Hz, $^3J_{15b,12} = 5.8$ Hz, $^2J_{15b,15a} = 10$ Hz, 2H; H(15b)), 2.51 (dd, $^3J_{12,15b} = 5.8$ Hz, $^4J_{12,10} = 5.8$ Hz, 2H; H(12)), 1.42 (d, $^2J_{15a,15b} = 10$ Hz, 2H; H(15a)), 1.4 (s, 6H; H(17)), 0.61 (s, 6H; H(16)); ^{13}C NMR (75.44 MHz, CD_3CN, 25 °C): $\delta = 163.1$ (q), 151.2 (q), 149.2 (C(1)), 148.8 (q), 148.2 (q), 142.9 (C(3)), 139.1 (C(8)), 127.4 (C(2)), 123.1 (C(4)), 121.1 (C(7)), 47.7 (C(13)), 46.6 (C(10)), 42.4 (C(12)), 42.1(C(11)), 32.0 (C(15)), 26.4 (C(17)), 21.0 (C(16)); CD (CH_3CN, 1.93×10^{-4} M, 0.1 cm cell): λ ($\Delta\varepsilon$) = 329 (−193), 304 (90); UV/Vis (CH_3CN, 1.93×10^{-4} M, 0.1 cm cell,): λ_{max} (ε) = 330 (sh, 2.4×10^4), 311 (3.5×10^4), 275 (sh, 1.6×10^4), 266 (2×10^4); MS (FAB, *m*-nitrobenzyl alcohol): *m/z* (%): 624 (100) $[M-NO_3]^+$, 562 (10) $[M-2NO_3]^{2+}$; elemental analysis (%) calcd for $ZnC_{34}H_{34}N_6O_6+1.5\,H_2O$: C 57.11, H 5.22, N 11.75; found: C 57.10, H 5.24, N 11.92.

[CdL1](ClO$_4$)$_2$: $Cd(ClO_4)_2\cdot 6H_2O$ (42 mg, 0.1 mmol) and **L1** (50 mg, 0.1 mmol) were stirred overnight at room temperature in chloroform/acetonitrile 1:1 (20 mL). The solvent was partially removed and the solution (2–3 mL) was filtered and precipitated by addition of diethyl ether. The precipitate was filtered off, dried, and analyzed (95%). ^{1}H NMR (300 MHz, CD_3CN, 25 °C): $\delta = 8.90$ (ddd, $^3J_{1,2} = 5.1$ Hz, $^4J_{1,3} = 1.6$ Hz, $^5J_{1,4} = 0.95$ Hz), 2H; H(1), 8.49 (d, $^3J_{4,3} = 9.2$ Hz, $^4J_{4,2} = 1.0$, $^5J_{4,1} = 0.95$, 2H; H(4)), 8.27 (d, $^3J_{7,8} = 8.0$ Hz, 2H; H(7)), 8.33 (ddd, $^3J_{3,4} = 9.2$ Hz, $^3J_{3,2} = 7.6$ Hz, $^4J_{3,1} = 1.6$ Hz), 2H; H(3), 7.87 (d, $^3J_{8,7} = 8.0$ Hz, 2H; H(8)), 7.84 (ddd, $^3J_{2,1} = 5.1$ Hz, $^3J_{2,3} = 7.6$ Hz, $^4J_{2,4} = 1.0$ Hz, 2H; H(2)), 3.85 (s, 2H; H(13)), 3.06 (dd, $^3J_{10,15b} = 5.5$ Hz, $^4J_{10,12} = 5.5$ Hz, 2H; H(10)), 2.90 (ddd, $^3J_{15b,10} = 5.5$ Hz, $^3J_{15b,12} = 5.5$ Hz, $^2J_{15b,15a} = 10.1$ Hz, 2H; H(15b)), 2.69 (dd, $^3J_{12,15b} = 6.0$ Hz, $^4J_{12,10} = 6.0$ Hz, 2H; H(12)), 1.54 (d, $^2J_{15a,15b} = 10.1$ Hz, 2H; H(15a)), 1.40 (s, 6H; H(17)), 0.59 (s, 6H; H(16)); ^{13}C NMR (75.44 MHz, CD_3CN, 25 °C): $\delta = 162.1$ (q), 151.0 (q), 150.8 (1), 148.8 (C(q)), 148.6 (q), 142.9 (C(3)), 138.9 (C(8)), 127.6 (C(2)), 124.6 (C(4)), 122.9 (C(7)), 48.6 (C(13)), 46.6 (C(10)), 42.7 (C(12)), 42.4 (q, C(11)), 32.1 (C(15)), 26.5 (C(17)), 21.0 (C(16)); CD (CH_3CN, 2×10^{-4} M, 0.1 cm cell): λ ($\Delta\varepsilon$) = 324 (−146), 299 (87), 270 (−20), 222 (34); UV/Vis (CH_3CN, 2×10^{-4} M, 0.1 cm cell,): λ_{max} (ε) = 321 (sh, 2.3×10^4), 307 (3.5×10^4), 273 (sh, 1.6×10^4), 264 (1.9×10^4); MS (ES): *m/z* (%) 711.1 (100) $[M-ClO_4]^+$, 306 (30) $[M-2ClO_4]^{2+}$; elemental analysis (%) calcd for $CdC_{34}H_{34}N_4Cl_2O_8+2\,H_2O$: C 48.27, H 4.53, N 6.62; found: C 48.25, H 4.38, N 6.67.

X-ray crystallography: Crystallographic and refinement details are given in Tables 1, 3, and 6. For [Cu**L1**Br](PF$_6$) cell dimensions and intensities were measured at 200 K on a Stoe Stadi4 diffractometer with graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å). Data were corrected for Lorentz and polarization effects and for absorption.[21] The structure was solved by direct methods using MULTAN 87,[22] the XTAL[23] system was used for all further calculations. The hydrogen atoms were included in calculated positions. All nonhydrogen atoms were refined anisotropically, using weighted full-matrix least-squares refinement based on *F*. The Flack parameter,[24] $x = 0.00(0)$, indicates that the coordinates correspond to the absolute structure of the molecule in the crystal. The PF_6 anions and acetonitrile molecules are located in channels parallel to the [010] direction and show no disorder. For the ligands and the remaining complexes the intensity data were collected at 223 K on a Stoe Image Plate Diffraction system using MoKα graphite monochromated radiation ($\lambda = 1.5418$ Å). The structures were solved by direct methods using the program SHELXS-97.[25] The refinement and all further calculations were carried out using SHELXL-97.[26] The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters (AFIX 137 for the methyl hydrogen atoms). The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. For all of the complexes the coordinates correspond to the absolute structure of the molecules in the crystals. The bond lengths and angles in the ligands and the complexes are close to expected values. In the crystal of [Ag**L1**](PF$_6$) half a molecule of water and one quarter of a molecule of diethyl ether per molecule of complex were located. These two molecules were refined isotropically and only the diethyl ether hydrogen atoms were included (calculated positions and as riding atoms). For [Pd**L2**](PF$_6$)$_2$ the space group $P3_1$ is enantiomorphously determining, hence it can be seen that the absolute structure of the molecule agrees with the stereochemistry of the ligand. In [Zn**L1**Zn**L2**](ClO$_4$)$_4$, space group $P1$, there are two independent molecules per unit cell together with two molecules of solvent of crystallization CH_3NO_2. In [Zn**L1**NO$_3$](NO$_3$) there are seven independent Zn^{II} complex molecules per asymmetric unit together with three molecules of acetonitrile (two of them having occupancies of 0.5), eleven water molecules (six having occupancies of 0.5) and one ether molecule (occupancy 0.5). The uncoordinated nitrate anions were refined with constraints on bond lengths and bond angles; the corresponding thermal factors were constrained to be equal. The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-142472: **L1**, CCDC-142473: **L2**, CCDC-142474: [Ag**L1**](PF$_6$)$_2$, CCDC-142475: [Pd**L1**](PF$_6$)$_2$, CCDC-142476: [Pd**L2**](PF$_6$)$_2$, CCDC-142477: [(Zn**L1**)$_2$OH](ClO$_4$)$_3$, CCDC-142478: [Zn**L1**Zn**L2**](ClO$_4$)$_4$, CCDC-142479: [Zn**L1**NO$_3$](NO$_3$), CCDC-142480: [(H$_2$O)Cd**L1**(μ-ClO$_4$)Cd**L1**-(ClO$_4$)][Cd$_2$**L1**$_2$(ClO$_4$)$_2$(μ-ClO$_4$)](ClO$_4$)$_3$, CCDC-142809: [Cu**L1**Br](PF$_6$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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