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Metal-Directed Assembly of Novel Helicating Ligands from 3-Oxa-1,5-diaminopentane and Acetone

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Template condensation of 3-oxa-1,5-diaminopentane (L^1) and acetone in the presence of cobalt(II), nickel(II), zinc(II), or cadmium(II) resulted in complexes of a new aminoethereal Schiff base ligand, 8,11,11-trimethyl-4,-14-dioxa-1,7,11,17-tetraazaheptadeca-7-ene (L^2). The reduction of the zinc(II) complex with L^2 using $LiAlH_4$ followed by treatment of alkaline solution gave free saturated N_4O_2 amino ether, 8,11,11-trimethyl-4,14-dioxa-1,7,11,17-tetraazaheptadecane (L^3). A complete structural determination was carried out for the $[CoL^2](ClO_4)_2$. Crystals are monoclinic, space group $P2_1/c$ with unit cell dimensions $a = 9.992(4)$, $b = 16.131(6)$, $c = 14.289(6)$ Å , $\beta = 98.85(2)°$, $V = 2276(2)$ Å^3, and $Z = 4$. Data were collected for 3899 reflections, giving final $R = 0.0715$ ($R_w = 0.0733$) for 332 parameters. The structure represents a rare skew-trapezoidal bipiramidal polyhedron with six-coordinate cobalt(II). Bond lengths Co−N are normal (average 2.10 Å), while distances Co−O are considerably longer (2.29−2.35 Å) attesting to weaker interactions. Primary amino groups of L^2 are located in trans positions, and overall ligand conformation is helical with intramolecular hydrogen bonds between protons of amino groups and alternate ether oxigen atoms of L^2.

Introduction

Molecular helicity, which is prevalent in many natural systems, has triggered vast recent studies on self-organization of oligomeric ligands into helical arrays in the presence of metal ions.[1] The scope of the synthetic systems varies from purely organic[2] to completely inorganic.[3] A metal-controlled formation of elegant double helices[4] and architecturally appealing triple helices[5] has been reported. The systems containing ligands with attached nucleic-acid bases display some structural features of DNA.[6] An initial helical subunit can be extended to an infinite helical complex due to association.[7] The principles governing formation of the multiple-helical structures are important in the design of artificial metalloproteins and polypeptides.[8]

Despite an extensive literature describing double and triple helices, surprisingly little is known about monohelical metal compounds,[9,10] the most fundamental models for natural α-helices. The chirality of monohelices is also of interest because of its potential applications in enantioselective catalysis. Stereoselective synthesis of octahedral complexes with predetermined helical chirality has been recently documented.[11]

Helical topology has been employed in the development of new metal-mediated syntheses. For instance, molecular knots

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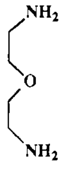
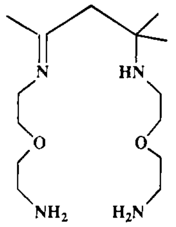
have been obtained from double-helical Cu(I) precursors.[12] In another example, intra-ligand carbon−carbon bond formation has been induced in a helical Ni(II) complex array.[13]

Usually, synthetic helices are generated in a multistep procedure.[14] Metal-mediated self-assembly typically requires rigorous correspondence between stereochemical preferences of the metal ion and coordinating possibilities of the ligand.[15] Organic synthesis of such specifically designed multidentates is often challenging. Therefore, ligand assembly from small, readily obtainable building blocks prior to their self-organization into helical arrays is particularly attractive. In such a process, the metal ion would play a double function of a template for both synthesis and helication. To the best of our knowledge, there are only two prior examples of the metal-assisted preparation of multidentates which form helices around the same metal ions.[9,16]

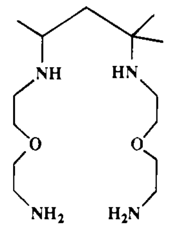
In this work, we report a metal-directed assembly of long-chain helicating aminoethereal ligands (L^2, L^3) from 3-oxa-1,5-diaminopenthane (L^1) and acetone. A preliminary communication of some of these results has appeared.[17]



L^1



L^2



L^3

Experimental Section

All materials were of reagent grade. Acetone and tetrahydrofurane (THF) were dried and distilled before use.

Syntheses. *Caution! Care must be exercised in handling all of the perchlorate complexes since they may be explosive upon heating.*

$[ML^1_2](ClO_4)_2$ (M = Co, Ni, Zn, Cd). $M(ClO_4)_2{\cdot}6H_2O$ (5.0 mmol) was dissolved in ethanol (25 cm^3) and 3-oxa-1,5-diaminopentane (10.0 mmol) was added. In 10−20 min formed products were isolated by filtration, washed subsequently with ethanol and ether, and air dried. Yield: 85−90%.

$[CoL^1_2](ClO_4)_2$. IR (Nujol): $\nu(NH_2)$, 3180, 3295, 3330 cm^{-1}. Electronic spectrum: ν_{max}, 19200 cm^{-1} (ϵ = 85), in methanol, c = 0.01 M. Anal. Calcd for $C_8H_{24}Cl_2N_4O_{10}Co$: C, 20.61; H, 5.19; N, 12.02; Co, 12.64. Found: C, 20.54; H, 4.79; N, 11.73; Co, 12.95.

$[NiL^1_2](ClO_4)_2$. IR (Nujol): $\nu(NH_2)$, 3190, 3300, 3350 cm^{-1}. Electronic spectrum: ν_{max}, 17160 cm^{-1} (ϵ = 18), 27280 cm^{-1} (ϵ = 36), in methanol, c = 0.01 M. Anal. Calcd for $C_8H_{24}Cl_2N_4O_{10}Ni$: C, 20.62; H, 5.19; N, 12.03; Ni, 12.60. Found: C, 20.35; H, 5.02; N, 12.31; Ni, 12.23.

$[ZnL^1_2](ClO_4)_2$. IR (Nujol): $\nu(NH_2)$, 3170, 3280, 3325 cm^{-1}. ^{13}C NMR (CD_3CN, δ): 40.3 (CH_2N); 68.5 (CH_2O). Anal. Calcd for $C_8H_{24}Cl_2N_4O_{10}Zn$: C, 20.33; H, 5.12; N, 11.86; Zn, 13.89. Found: C, 20.90; H, 5.00; N, 11.94; Zn, 14.20.

$[CdL^1_2](ClO_4)_2$. IR (Nujol): $\nu(NH_2)$, 3180, 3300, 3350 cm^{-1}. ^{13}C NMR (CD_3CN, δ): 40.6 (CH_2N); 68.1 (CH_2O). Anal. Calcd for $C_8H_{24}Cl_2N_4O_{10}Cd$: C, 18.49; H, 4.66; N, 10.78; Cd, 21.64. Found: C, 18.46; H, 4.40; N, 10.54; Cd, 21.50.

$[ML^2](ClO_4)_2$ (M = Co, Ni, Zn, Cd). $M(ClO_4)_2$ (5.0 mmol) was dissolved in 150 cm^3 of dry acetone and L^1 (1.04 g, 10 mmol) was added. For M = Co, Ni, the mixture was heated in sealed tube for 3 h at 100 °C. In the case of M = Zn, Cd, the solution was refluxed for 5 min. After the removal of the solvent, the residue was washed with ethanol and air dried. If oily products were formed, they were first treated with ether followed by ethanol washing. Yield: 80−90%.

The results were essentially the same when $[ML^1_2](ClO_4)_2$ in place of $M(ClO_4)$ and 3-oxa-1,5-diaminopentane was introduced to react in dry acetone.

$[CoL^2](ClO_4)_2$. IR (Nujol): $\nu(NH_2)$, 3190, 3280, 3320 cm^{-1}; ν(NH), 3240 cm^{-1}; ν(C=N), 1655 cm^{-1}. Electronic spectrum: ν_{max}, 19400 cm^{-1} (ϵ = 140), in methanol, c = 0.01 M. Anal. Calcd for $C_{14}H_{32}Cl_2N_4O_{10}Co$: C, 30.78; H, 5.90; N, 10.26; Co, 10.79. Found: C, 30.85; H, 6.14; N, 9.84; Co, 10.84.

$[NiL^2](ClO_4)_2$. IR (Nujol): $\nu(NH_2)$, 3195, 3300, 3350 cm^{-1}; ν(NH), 3260 cm^{-1}; ν(C=N), 1665 cm^{-1}. Electronic spectrum: ν_{max}, 17760 cm^{-1} (ϵ = 23), 27360 cm^{-1} (ϵ = 37), in methanol, c = 0.01 M. Anal. Calcd for $C_{14}H_{32}Cl_2N_4O_{10}Ni$: C, 30.80; H, 5.91; N, 10.26; Ni, 10.75. Found: C, 30.33; H, 6.08; N, 10.62; Ni, 11.32.

$[ZnL^2](ClO_4)_2$. IR (Nujol): $\nu(NH_2)$, 3190, 3280, 3320 cm^{-1}; ν(NH), 3240 cm^{-1}; ν(C=N), 1660 cm^{-1}. ^{13}C NMR (CD_3CN, δ): 21.1, 23.5, 26.9 (3 Me); 39.1, 39.6, 41.5 (CH_2N); 50.2 (CCH_2C); 55.1 (Me$_2$C); 67.3, 67.8 (CH_2O); 185.6 (C=N). Anal. Calcd for $C_{14}H_{32}Cl_2N_4O_{10}Zn$: C, 30.42; H, 5.84; N, 10.14; Zn, 11.83. Found: C, 30.21; H, 5.30; N, 10.42; Zn, 11.60.

$[CdL^2](ClO_4)_2$. IR (Nujol): $\nu(NH_2)$, 3180, 3270, 3320 cm^{-1}; ν(NH), 3230 cm^{-1}; ν(C=N), 1660 cm^{-1}. ^{13}C NMR (CD_3CN, δ): 20.7, 23.0, 27.3 (3 Me); 40.0, 40.2, 41.6 (CH_2N); 50.8 (CCH_2C); 55.3 (Me$_2$C); 68.1, 68.6 (CH_2O); 182.1 (C=N). Anal. Calcd for $C_{14}H_{32}Cl_2N_4O_{10}Cd$: C, 28.04; H, 5.38; N, 9.34; Cd, 18.74. Found: C, 28.26; H, 5.20; N, 9.20; Cd, 18.99.

$[ZnL^3](ClO_4)_2$. To a solution of $LiAlH_4$ (0.38 g, 10.0 mmol) in anhydrous THF (150 cm^3) in Ar-atmosphere $[ZnL^2](ClO_4)_2$ (2.76 g, 5.0 mmol) was added gradually. The mixture was stirred for 2 h followed by dropwise addition of water to quench the access of $LiAlH_4$. The precipitate was separated and washed with hot acetonitrile (30 cm^3) for 3 times. The filtrate was evaporated to dryness, the residue was washed with ether and ethanol, and air dried. Yield: 1.91 g, 69%.

IR (Nujol): $\nu(NH_2)$, 3180, 3275, 3320 cm^{-1}; ν(NH), 3230 cm^{-1}. ^{13}C NMR (CD_3CN, δ): 20.0, 22.2, 27.5 (3 Me); 39.0, 40.1, 40.3, 42.5 (CH_2N); 45.6, 49.4 (MeCH); 51.1 (CCH_2C); 56.4 (Me$_2$C); 66.9, 67.3, 68.0, 68.2 (CH_2O). Anal. Calcd for $C_{14}H_{34}Cl_2N_4O_{10}Zn$: C, 30.31; H, 6.17; N, 10.10; Zn, 11.78. Found: C, 30.14; H, 6.35; N, 10.49; Zn, 11.51.

Isolation of Free Ligand L^3. The complex $[ZnL^3](ClO_4)_2$ (1.66 g, 3.0 mmol) was placed into Sohxlet apparatus containing solution of sodium hydroxide (40 g) in water (30 cm^3). After refluxing for 3 h the solid complex was completely dissolved and transferred into alkaline solution. The mixture was extracted by ether (10 cm^3, 5 times). Ether solution was dried by NaOH followed by solvent evaporation to give L^3. Yield: 0.73 g, 84%.

IR (neat): ν(NH), 3280, 3380 cm^{-1}; $\delta(NH_2)$, 1600 cm^{-1}; ν(COC), 1150 cm^{-1}. ^{1}H NMR (CD_3CN, δ): 0.97 (d, 3H, CH_3), J = 6.2 Hz; 1.04, 1.10 (s + s, 6H, $(CH_3)_2C$); 1.18, 1.26 (d + d, 2H, CCH_2C); 1.96 (s, 6H, NH_2 + NH); 2.73 (t, 8H, CH_2N); 3.38, 3.47 (t + t, 8H, CH_2O). Mass spectrum: m/e 145 ($M^+/2$), 154, 187, 214. Anal. Calcd for $C_{14}H_{34}N_4O_2$: C, 57.89; H, 11.80; N, 19.29. Found: C, 57.64; H, 11.92; N, 19.49.

Condensation of 3-Oxa-1,5-diaminopentane and Acetone. 3-Oxa-1,5-diaminopentane (10.0 mmol) was dissolved in dry acetone (150 cm^3) and heated in sealed tube for 3 h at 100 °C. The solvent was removed, and the residue was distilled under vacuum to afford 2,10-dimethyl-6-oxa-3,9-diaza-undeca-2,9-diene (L^4) as a yellowish oil, 76%, bp 90 °C (0.3 Torr). NMR ($CDCl_3$, δ): 1.88, 2.04 (s + s, 12H, $(CH_3)_2C$); 3.43 (t, 4H, CH_2N), 3.75 (t, 4H, CH_2O). Mass spectrum:

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Table 1. Experimental Crystallographic Data for $[CoL^2](ClO_4)_2$

formula	$CoCl_2O_{10}N_4C_{14}H_{32}$
fw	546.3
cryst system	monoclinic
space group	$P2_1/c$
a, Å	9.992(4)
b, Å	16.131(6)
c, Å	14.289(6)
β, deg	98.85(2)
V, Å^3	2275.7(16)
Z	4
D_{calcd}, g cm^{-3}	1.594
abs coeff, mm^{-1}	1.043
μ, cm^{-1}	10.4
F(000)	1146
radiation	Mo Kα (λ = 0.710 69 Å)
temp, °C	−120
$R(F)$	0.0715
$R_w(F)$	0.0733

m/e 185 ($M^+ + 1$), 128, 102, 84, 70. Anal. Calcd for $C_{10}H_{20}N_2O$: C, 65.18; H, 10.94; N, 15.20. Found: C, 65.24; H, 10.85; N, 15.01.

Attempted Reaction of 3-Oxa-1,5-diaminopentane Hydroperchlorate ($L^1{\cdot}HClO_4$) and Acetone. 3-Oxa-1,5-diaminopentane hydroperchlorate, prepared similarly to the known precedent,[18] was treated with acetone as in the previous experiment. The solution turned dark brown and only tarry aldol condensation products were observed upon cooling.

Spectroscopic Measurements. The IR spectra in the region 400−4000 cm^{-1} were obtained on a M-80 spectrometer (Carl Zeiss, Jena, Germany) using KBr pellets. The UV−vis spectra were recorded on a M-40 spectrometer (Carl Zeiss, Jena, Germany) using 1.0 cm quartz cells. The ^{1}H and ^{13}C NMR analyses were done on a WP-200 (Bruker) instrument. The mass-spectra were measured on a Ribermag P10-10B (Nermag, France) spectrometer.

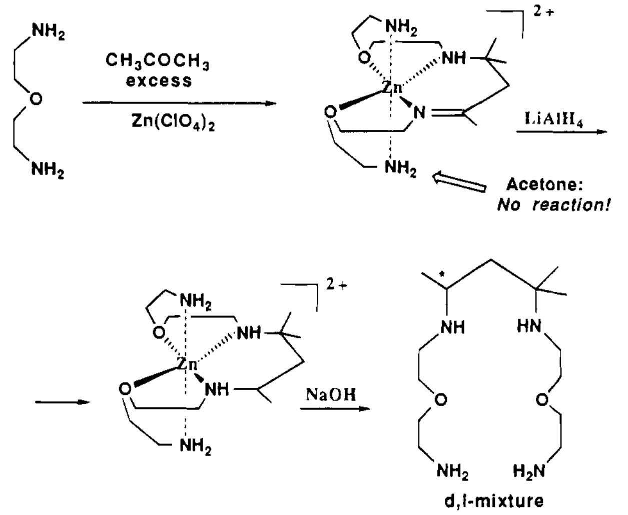
Crystallography. The single crystal of $[CoL^2](ClO_4)_2$ was obtained from 1:1 acetonitrile−ethanol mixture. Crystals formed in about 4 days.

The experimental parameters for $[CoL^2](ClO_4)_2$ are summarized in Table 1. The X-ray intensity data were collected with an automatic four-circle Syntex P2$_1$ diffractometer at 153 K using graphite monochromated MoKα radiation. The unit cell parameters were determined on the basis of accurately refined positions of 24 reflections in the 13 $\leq \theta \leq$ 14° interval. The intensities of 3899 reflections (3554 symmetrically independent) were measured using the $\theta/2\theta$-scan (background coefficient 0.25) in the q range from 2.0 to 30.0° with a variable scan speed (3.0 to 30.0°/min in ω). The intensities of two standard reflections (measured every 98 reflections) did not show any essential changes.

All calculations were performed with an IBM-PC/AT computer using Siemens SHELXTL PLUS programs (PC version). After Lorentz and polarization corrections were performed, the intensities of 3286 observed $\{F > 6.0\sigma(F)\}$ reflections were used. The absorption correction was not applied (μ = 10.4 cm^{-1}). The structure was solved using direct methods and refined by full-matrix least squares in the isotropic approximation. The disorder of the N(7), C(10), C(15), C(16), and C(20) atoms of the complex cation and all oxygen atoms in both counterions were detected in the subsequent difference Fourier map, and the occupancy factors $^2/_3$ and $^1/_3$ were empirically adjusted for each pair of position of these atoms. Finally, all non-hydrogen atoms with the exception of those with the $^1/_3$ occupancy factor were refined anisotropically. In the last set of difference syntheses almost all H-atoms were located, but only some of them (those not involved in the disordered moiety) could be successfully refined (with fixed U_{iso} = 0.06 Å^2).

Results and Discussion

Synthesis. A new unsymmetrical multidonor amino ether,L^3, has been assembled from easily available building blocks using the following reaction sequence:

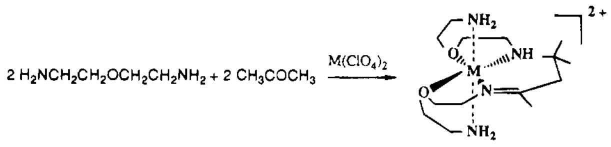


We have reported single crystal X-ray structures of the helical zinc complexes previously.[17] Only one L^1 amino group condenced with acetone. *Trans* location of terminal amino groups in the formed ligands provided unusual *spatial* and *coordination* protection and prevented further reaction with acetone. Precedents for mono N-functionalization of polyamines coordinated to metal ion are very rare.[19]

Condensation of L^1 with acetone yielded the expected Schiff base, L^4, in contrast to the same reaction in the presence of metal ions:

$$H_2NCH_2CH_2OCH_2CH_2NH_2 + 2CH_3COCH_3 \rightarrow (CH_3)_2C{=}NCH_2CH_2OCH_2CH_2N{=}C(CH_3)_2$$

Thus, reaction of 3-oxa-1,5-diaminopentane with acetone in the presence either Zn(II), Co(II), Ni(II), or Cd(II) led to the surprisingly clean isolation of complexes of acyclic product L^2:



(1)

There was a wide variation in the reaction time required for the metal-mediated condensations. For M = Co(II), Ni(II), for example, the template condensation (1) required heating at 100 °C for 3 h. In the case of M = Zn(II), Cd(II) the reaction was complete after refluxing for 5 min. With Cu^{2+}, condensation gave a labile product which decomposed quickly after isolation as evidenced by its IR spectrum.

The mechanism of transformation (1) presumably involves initial formation of metal complexes with L^1 in ratio 1:2, followed by condensation with acetone to the corresponding Schiff base products. Indeed, compounds $[ML^1{}_2](ClO_4)_2$ were isolated in the absence of acetone, and their subsequent reaction with acetone led to $[ML^2](ClO_4)_2$ products.

Reported by Curtis classical ethylenediamine condensations with acetone[20] occurred for both protonated and metal ion complexed amine to form the same macrocyclic product, so that a metal center did not appear to provide a critical stereochemical role.[21] However, reaction (1) is clearly a metal-templating condensation since a different reaction occurs in the absence of the metal ions with either free or protonated amine. Two complementary roles for a template have recently been described: a positive template effect which bring two reactive

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ends of the same molecule together, assisting intramolecular reaction, and a negative template effect which hold the ends apart, inhibiting intramolecular interaction.[22] Actually, these roles are manifestations of a kinetic template effect.[23] The present template syntheses yield examples of both such effects: a positive effect on the facilitation intramolecular condensation of two aminoethereal ligands and a negative effect on keeping the terminal amino groups sufficiently isolated to preclude further reactions.

In contrast to azacompounds,[20] amino ether Schiff base complexes are hydrolytically unstable in solvents other than acetone. This trend was most pronounced for the cadmium complex, which decomposed at room temperature, giving the starting complex and 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol):

$$[\mathrm{CdL}^2]^{2+} + \mathrm{H_2O} \xrightarrow{\mathrm{CH_3CN}} [\mathrm{CdL}^1{}_2]^{2+} + (\mathrm{CH_3})_2\mathrm{C(OH)CH_2COCH_3}$$

Lithium alumohydride reduction of the zinc Schiff base complex and subsequent treatment with alkali liberated free L^3 due to the relative weakness of the $[ZnL^3]^{2+}$ complex and the amphoterous nature of Zn^{2+}. L^3 in the reduced Zn complex also did not show any transformations in acetone solution similar to the precursor Zn compound. However, both terminal amino groups of the free L^3 readily reacted with acetone in an expected way to form the corresponding Schiff base.

Characterization and Solution Properties. All compounds were characterized by elemental analysis and IR spectra. New bands appearing at 3230−3260 cm^{-1} and 1655−1665 cm^{-1} in the IR spectra of $[ML^2]^{2+}$ complexes were assigned to the secondary amino group of L^2, ν(NH), and the new double bond C=N, ν(C=N), respectively. On reduction, the latter band disappeared, while other signals of $[ZnL^3](ClO_4)_2$ remained similar to those of the precursor Schiff base complex. For all complexes, perchlorate absorption occurred 625 cm^{-1} and 1100 cm^{-1} pointing out their out-of-sphere nature.

The transition metal complexes contain hexacoordinate M^{2+} as evidenced by their electronic spectra in solution. Indeed, complexes of cobalt(II) display similar features ($^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition) as those of the N_4O_2 donor set containing macrocyclic ligands.[24] The Ni(II) complexes show two bands in the visible region falling well within the range of octahedral nickel complexes with similar ligands,[25] and are assignable to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions. In general, the d−d transitions of the L^1 complexes occur at 200−600 cm^{-1} lower energy than those of L^2.

^{13}C NMR spectra of coordinated ligands in Zn and Cd complexes were analogous attesting to their similar geometry. For the cobalt complex with L^2, the X-ray crystal structure has been solved and is presented below.

Structure of Cobalt(II) Complex $[CoL^2](ClO_4)_2$. The molecular structure of the $[CoL^2]^{2+}$ ion and its space-filling representation are shown in Figure 1. The selected atomic coordinates are listed in Table 2; relevant bond distances and angles are given in Table 3.

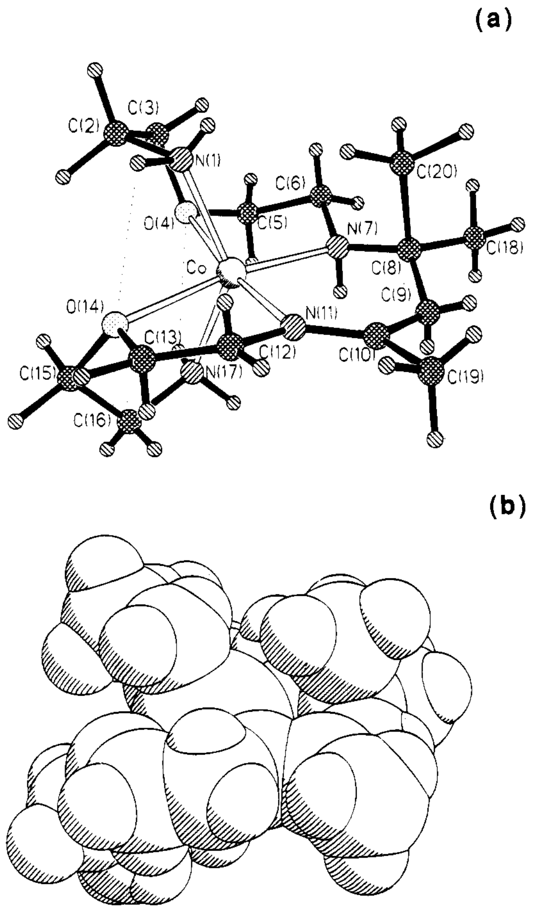

Figure 1. (a) View of Λ-$[CoL^2]^{2+}$ cation (*S*-diastereomer) showing the atomic numbering scheme. Coordination bonds are designated by thin solid lines. Intramolecular hydrogen bonds are drawn in dotted lines. (b) Space-filling representation of the same molecule.

Table 2. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	y	z	$U_{eq}{}^a$
Co	7503(1)	5376(1)	2126(1)	39(1)
N(1)	8083(6)	4130(3)	2315(3)	45(2)
C(2)	7366(9)	3606(4)	1533(5)	59(3)
C(3)	5893(8)	3733(4)	1487(5)	59(3)
O(4)	5650(5)	4622(3)	1339(3)	60(2)
C(5)	4513(8)	4919(5)	1714(6)	65(3)
C(6)	4853(8)	5078(5)	2769(6)	67(3)
N(7)	6009(10)	5626(8)	2999(8)	35(3)
C(8)	6377(10)	5936(5)	3860(6)	74(3)
C(9)	7534(9)	6518(5)	4030(5)	62(3)
C(10)	8927(13)	6428(8)	3750(8)	57(4)
N(11)	9036(6)	6035(3)	2980(4)	45(2)
C(12)	10332(9)	5896(9)	2681(7)	102(5)
C(13)	10397(11)	5678(8)	1779(9)	116(6)
O(14)	9222(5)	5333(3)	1237(3)	56(2)
C(15)	8667(17)	5654(9)	281(8)	72(5)
C(16)	7717(19)	6338(9)	326(11)	66(6)
N(17)	6854(8)	6171(4)	974(5)	74(3)
C(18)	5268(10)	6156(6)	4394(6)	85(4)
C(19)	9998(10)	6818(8)	4393(7)	105(5)
C(20)	7279(14)	5071(8)	4394(8)	72(5)

[a] U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The organic ligand functions as a hexadentate chelate through its four nitrogens and two oxygens. The Co-N distances (average 2.10 Å) are at the short end of the range (2.10−2.20 Å) expected for such bonds in Co(II) complexes with conventional ligands.[26] On the contrary, Co-O bond lengths (2.289 and 2.352 Å) are considerably longer and compare favorably

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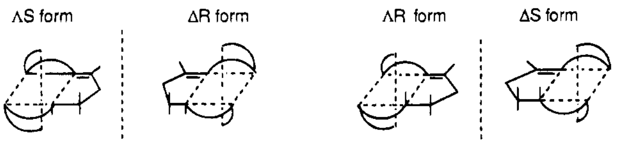
Table 3. Relevant Bond Distances (Å) and Angles (deg)

	Distances		
Co−N(1)	2.098(5)	O(4)−C(5)	1.451(14)
Co−N(11)	2.095(5)	N(7)−C(8)	1.327(14)
Co−N(17)	2.109(7)	C(10)−N(11)	1.289(13)
Co−O(4)	2.352(5)	N(11)−C(12)	1.442(11)
Co−O(14)	2.289(5)	C(13)−O(14)	1.417(12)
N(1)−C(2)	1.492(9)	O(14)−C(15)	1.486(12)
C(3)−O(4)	1.465(9)	C(16)−N(17)	1.385(20)
	Angles		
N(1)−Co−O(4)	75.4(2)	O(4)−Co−N(17)	79.4(2)
N(1)−Co−N(7)	108.1(4)	N(7)−Co−N(11)	94.5(3)
N(1)−Co−N(11)	104.4(2)	N(7)−Co−O(14)	170.4(3)
N(1)−Co−O(14)	80.0(2)	N(7)−Co−N(17)	100.6(4)
N(1)−Co−N(17)	136.8(2)	N(11)−Co−O(14)	72.2(2)
O(4)−Co−N(7)	78.8(3)	N(11)−Co−N(17)	104.8(2)
O(4)−Co−N(11)	172.8(2)	O(14)−Co−N(17)	75.6(2)
O(4)−Co−N(14)	108.8(2)		
	Torsion Angles		
O(4)−C(3)−C(2)−N(1)	57.7	C(12)−N(11)−C(10)−C(9)	−177.7
O(4)−C(5)−C(6)−N(7)	54.3	O(14)−C(13)−C(12)−N(11)	−20.2
C(6)−N(7)−C(8)−C(9)	−172.9	N(17)−C(16)−C(15)−O(14)	−43.0

with the similar Co-O distances (2.317 and 2.339 Å) found previously for an octahedral Co^{2+} complex with a mixed N,O-acyclic ligand.[27]

Interestingly, L^2 ligand wraps around the Co^{2+} ion to form an overall helical conformation (Figure 1 b). Different ligating capabilities of the nitrogen and oxygen atoms along with the ligand shape result in high degree of complex distortion to give a skew-trapezoidal bipiramidal polyhedron, a rare type of geometry[28] which is unprecedented for a hexadentate ligand. The two ethereal oxygens together with both imino and secondary amino groups occupy the equatorial plane, while the primary amino groups comprise apical positions. The axial atoms are displaced towards the most elongated O••O edge (angle N(1)CoN(17) is 138.8° instead of 180° in ideal octahedron and angle O(4)CoO(14) is 108.8° instead of 90°).

Since two directions for the helix are possible, the centrally coordinated Co(II) ion becomes a chiral center affording two absolute configurations. These are designated as Λ and Δ in analogy with octahedral complexes with three chelate rings.[29] Additional chirality appears as a result of the coordination of the secondary amino group to Co^{2+} which gives rise to different stereoisomers depending on whether the hydrogen on the N atom is above or below the equatorial plane. In the present instance, there are two pairs of diastereomers:



Even though starting materials are achiral, the possibility for a diastereoselective reaction exists if one pair of enantiomers is formed in an excess. For [ZnL^2]$^{2+}$ all four stereoisomers were found to be present in equal amounts in the crystal.[17] However, for the corresponding cobalt(II) complex one of the pair of diastereomers, ΛS and ΔR *versus* ΛR and ΔS, respectively, was formed predominantly in the approximate ratio of 2 to 1. Indeed, in the case of the Co(II) complex, the geometrical demands of the metal ion resulted in some changes of the overall structure leading to a noticable strain for the ΛR diastereomer as well as for its enantiomer. The effect is especially pronounced for the six-membered chelate rings. The *chair* forms are found in both diastereomers, though the extent of their distortion is somewhat different. Firstly, the deviations of C(10*) and C(9) atoms from the mean CoN(7)C(8)N(11) plane for the ΛR isomer are 0.50 and −0.42 Å , respectively (the corresponding values for ΛS isomer are 0.26 and −0.18 Å). Second, the C═N double bond twist for the ΛR isomer deviates from 180° by 7.1°, the corresponding value being 2.3° for the ΛS isomer as follows from the torsion angles values (Table 3). It is not surprising, therefore, that the complex reported here adopts preferentially the ΛS (and ΔR) configuration. In contrast, the same cobalt(II) six-membered chelate segment exhibits *sofa* conformation when incorporated into a macrocycle, the deviation of the C(CH$_3$)$_2$ from the least-squares plane of the other atoms being 0.60 Å .[30]

In [CoL^2]$^{2+}$, the primary amine hydrogens participate in the intramolecular hydrogen bonding to the ether oxygens, evidenced by N(1)H••O(14) and N(17)H••O(4) bond distances of 2.824 and 2.855 Å, respectively (the analogous distances in Zn^{2+} complexes are 2.870–2.956 Å[17]). There are only two shortened intermolecular contacts, viz. N(17)••O(2.2) and N(17)••O(1x), 2.895 and 2.826 Å, correspondingly. The observed disorder for both perchlorate anions with occupancy ratio 2:1 correlating with that for the ΛS and ΛR diastereomers, strongly supports perchlorate interactions in the crystal with isomeric complex cations.

Conclusion

We found and structurally characterized two novel mononucleating multidentate ligands which adopt a monohelical coordination in the solid state. Template assembly of one of the ligands from simple building blocks and helication around the same metal ion proceeded cleanly and showed diastereoselectivity. Prior examples of noncyclic template condensations involving the same building block L^1 did not show similar features.[27,31]

Three factors judged important to the ultimate success of the template synthesis: (i) the ability of the metal ion to simultaneously bind ligands' amino nitrogen and ether oxygen donor atoms; (ii) the initial formation of a metal complex of stoichiometry M:L^1 = 1:2; (iii) a "tetrahedral distortion" from the octahedron about the cobalt(II), nickel(II), zinc(II), and cadmium(II) centers.

The most interesting structural feature in the new complexes is their helical ligand coordination. In principle, several options for coordination are possible for a hexadentate ligand. For the present complexes, the match between favored metal ion stereochemistry and coordinating possibilities of ligands is achieved only by helication. As shown for Zn complexes, helical coordination is maintained upon L^2 → L^3 transformation supporting the view that helicity in these complexes depends largely on general ligand design and is essentially insensitive to minor changes in the ligand structure.

The coordinating primary amino groups of the complexes are located at sites substantially remote from each other precluding further condensation with acetone which might result in ring closure. Compound L^3 is "a conceptual intermediate" which could be readily resolved into enantiomers. The present template synthesis of L^3 is vastly preferred over conventional

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nontemplate routes to the same ligand.

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Supplementary Material Available: Listings of crystal data, data collection, and solution and refinement, all bond lengths and bond angles, anisotropic displacement coefficients, all atomic including hydrogen atom coordinates and isotropic displacement coefficients, and torsion angles (12 pages). Ordering information is given on any current masthead page.