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Preparation of Monometallic Complexes of Non-Macrocyclic Ligands

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Dicompartmental non-macrocyclic ligands containing six (N_4O_2) and four (N_2O_2) coordination atoms were prepared. The ligands were constructed in order to investigate the effect of an opened four-coordination site (non-marcocyclic effect) on the geometrical structure of a complex in a six-coordination site with a labile metal. In this regard, monometallic non-macrocyclic complexes of Zn(II), Co(II), and Co(III) were prepared and characterized. The preparation of a Co(III) complex through two different routes, and also the X-ray crystal structure of a Zn(II) complex demonstrated that the structures of the complexes were intact even in the presence of two bulky phenyl groups in four-coordination site. The characterization of the prepared complexes confirmed the presence of two protons in the four-coordination site of diimine complexes and a lack of them in diamine complexes.

The chemistry of metal complexes with dicompartmental ligands has become a rapidly growing area of research, because of their importance in biomimetic studies of binuclear metalloproteins, their interesting catalytic properties, their ability to stabilize unusual oxidation states and mixed-valance compounds, and possibilities for a magnetic interaction between the two metal ions, leading to the design of molecular magnetic materials.[1–4] Mono- and bimetallic complexes of macrocyclic ligands of type 1 have been prepared, and their structures and reactivities investigated by Bosnich,[5–10] Busch,[11] and us.[12,13] Such ligands contain two compartments: one includes six coordination atoms (N_4O_2), and the other has a tetradentate N_2O_2 donor set. The two metals are bridged by phenolic oxygen ligands, and the two compartments are completed by two links, a close-site link and an open-site link (Chart 1). The effect of an open-site link on the geometry of the metal on the 6-coordinate site of macrocyclic complexes was investigated, and showed that an open-site linkage influences the structural geometry of metal in a 6-coordinate site.[14] Based on our knowledge, such investigations have not been employed on any non-macrocyclic ligand. The propose of this work was to investigate the stereochemistry of metal in a 6-coordinate site of a non-macrocyclic system. The ligands chosen for this investigation were L^2 and L^3, which can be prepared from monometallic complexes of ligand L^1. These ligands are shown in Scheme 1.

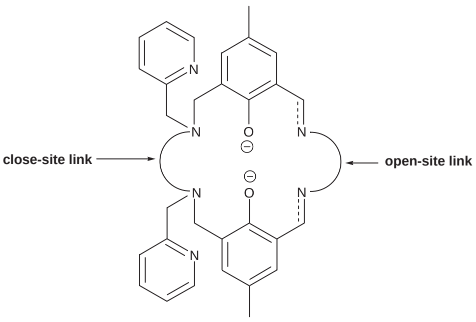

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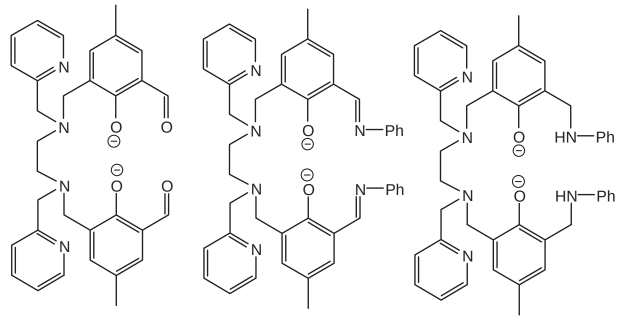
Chart 1.



L^1 L^2 L^3

Scheme 1. Non-macrocyclic dicompartmental ligands.

Results and Discussion

Synthesis. Monometallic zinc(II) and cobalt(II) complexes were prepared by the methods outlined in Fig. 1. Compounds Li_2L^{17} and ML^{110} were prepared by published procedures and used as starting materials to prepare monometallic complexes ML^2 and ML^3. The reaction of ML^1 with two equivalents of aniline under acid catalysis[10] resulted in monometallic diprotonated ML^2 complexes that were separated as solids from solution by the addition of saturated NH_4PF_6. The solid spin-free $Co^{II}L^2$ complex was indefinitely stable in air, but slowly oxidized in air when dissolved in CH_3CN solution (Fig. 1).

The characterization results of the diamagnetic ZnL^2 complex by ^1H NMR indicated the presence of two protons in the N_2O_2 cavity, as was observed for its analogous macrocyclic complexes.[9] The corresponding amine complexes were prepared by BH_4^- reduction of the imine compounds. In this way, ZnL^3 and CoL^3 were prepared as solids. Unlike the corresponding imine complexes, the presence of the protons was

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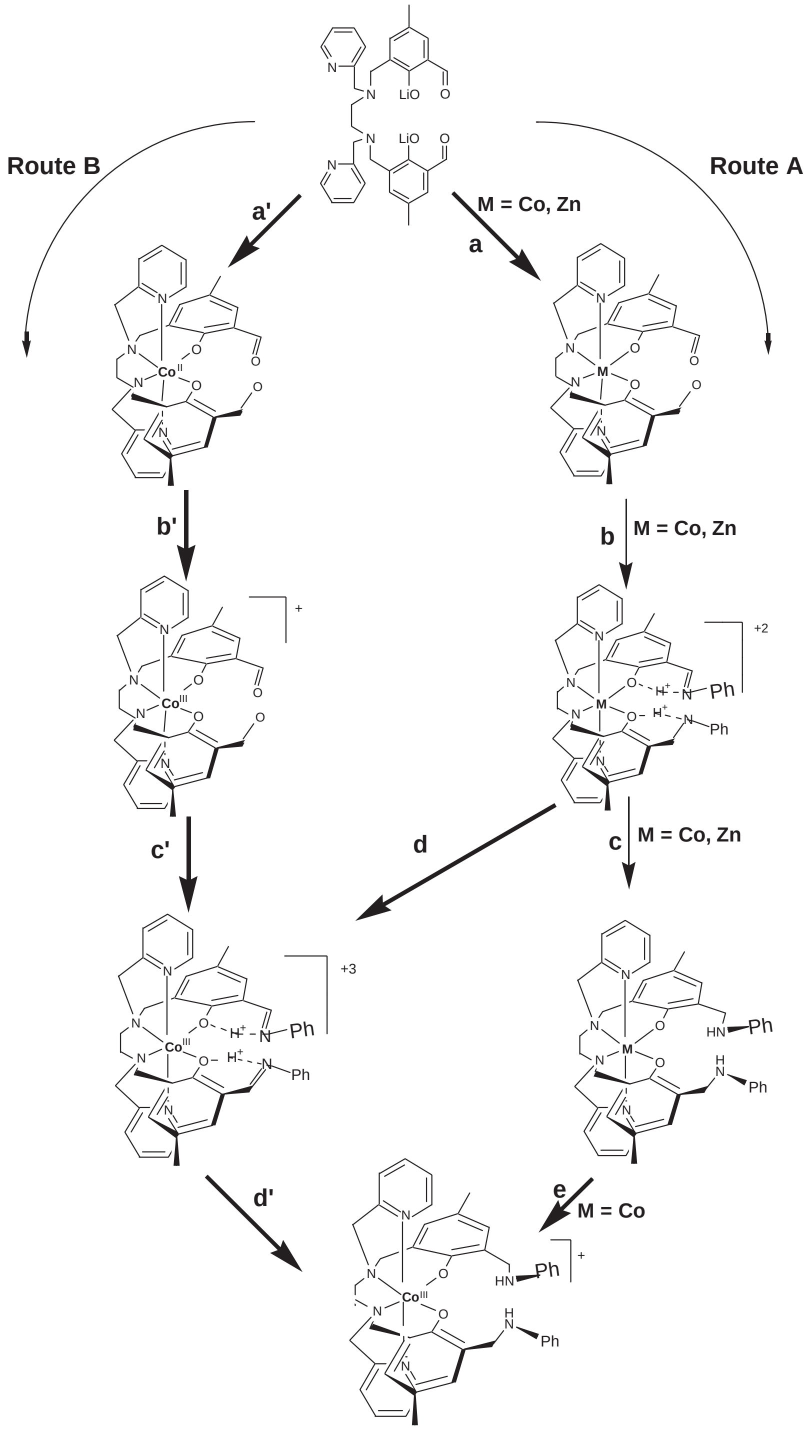
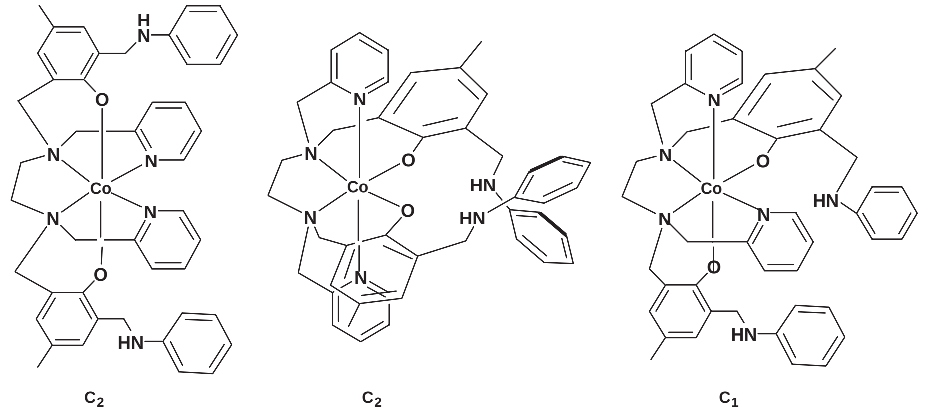


Fig. 1. Synthetic transformations. The following reagents/solvents were used. Reaction a, a′, and b′: see Ref. 10. Reaction b: $PhNH_2$ and HOAc; MeOH. Reaction c: $NaBH_4$; CH_3CN. Reaction d and e: ferrocenium ion; CH_3CN. Reaction c′: $PhNH_2$ and HOAc; CH_3CN. Reaction d′: $NaBH_4$; CH_3CN.

not observed in the N_2O_2 cavity of the amine complexes and complexes were neutral and almost insoluble in common solvents. The ^{1}H NMR spectrum of the diamagnetic complex $[Co^{III}L^3]^+$ indicated that the structure possesses C_2 symmetry in solution. There are three possible topological isomers for complexes type ML^2 and ML^3,[8] as shown in Scheme 2. Two of these possess C_2 symmetry, whereas the third is an unsymmetrical C_1 isomer with cis-disposed pyridines and *cis*-phenolates. C_2 symmetrical isomers correspond to either *cis*-pyridines and *trans*-phenolates or *trans*-pyridines and *cis*-phenolates. To investigate the structures of ML^2 and ML^3 in solution, two different routes to prepare $[Co^{III}L^3]^+$ were carried out. In route A (Fig. 1), first the dialdehyde complex $[Co^{II}L^1]$ was prepared,[10] which was then converted to the diimine compound $[Co^{II}L^2(H^+)_2]^{2+}$ by two equivalents of aniline. In the next step, the $[Co^{II}L^2(H^+)_2]^{2+}$ was oxidized to



Scheme 2. Different possible topological isomers for $[CoL^3]^+$.

$[Co^{III}L^2(H^+)_2]^{3+}$ by ferrocenium ions (Fc^+). Finally, the resulting diimine complex was reduced to its diamine counterpart, $[Co^{III}L^3]^+$, by a reducing agent of $NaBH_4^-$. Alternatively, in route B (Fig. 1) the prepared $Co^{II}L^1$ was oxidized to $[Co^{III}L^1]^+$ by Fc^+. This compound was then reacted with two equivalents of aniline to obtain $[Co^{III}L^2(H^+)_2]^{3+}$ as a dark-green solid upon the addition NH_4PF_6. Finally, the diimine cobalt(III) complex was reduced to its diamine counterpart by $NaBH_4$. Since $[Co^{III}L^1]^+$ was proved to be stable against isomerization, and also its structure was determined to have a C_2 symmetry structure with *trans*-pyridines and *cis*-phenolates,[10] it was used as a starting material to prepare of $[Co^{III}L^2(H^+)_2]^3$ and $[CoL^3]^+$. The identification of $[CoL^3]^+$, obtained through the two routes, implies that isomerization is less likely to occur under the condition used to perpare of ML^2 and ML^3, and confirmed that presence of two bulky phenyl groups in the open-site dose not influence the structural geometry of metal in the close-sit, even with a labile metal, such as Co(II) and Zn(II). As a result, these complexes have structures with *trans*-pyridines and *cis*-phenolates.

All attempts to accommodate metal into the N_2O_2 cavity of monometallic complexes ML^2 and ML^3 were not successful, but resulted in a recovery of the starting materials. The major factor in our inability to form bimetallic complexes may be due to a steric-repulsion of the N-Ph groups so that the N-Ph moieties are tilted above and below the mean molecular plane and the bite angles associated with the N_2 (imine or amine) are expanded. As a result the second metal can not bind to the N_2O_2 coordinating atoms. This conclusion was confirmed by the crystal structure of ZnL^2, which we now discuss.

Physical Characterization. All imine complexes of $[M^{II}L^2(H^+)_2]^{2+}$ are soluble in polar solvents, such as acetonitrile and acetone, and show 2:1 electrolytes in an acetonitrile solution. However, bivalent metal complexes of type ML^3 are insoluble in all common solvents. The characterization of these complexes reveals a lack of protons in the N_2O_2 cavity of the ML^3 complexes, whereas the ML^2 complexes do show the presence of two protons in the N_2O_2 cavity. The protonated monometallic complexes of the macrocyclic binucleating ligand have previously been reported.[15] Bosnich and co-workers reported that each proton in the N_2O_2 cavity interacts with oxygen of the phenolate and the nitrogen of the imine or amine moieties.[9] As a result, the absence of protons in the N_2O_2 cavity of the ML^3 complexes could be due to a greater flexibility of the amine compounds compared with their imine counterparts, which result in more twisting of the phenyl groups and the amine nitrogens, so that hydrogen bonding might not be achieved between the oxygens of the phenolic groups and the nitrogens of the amine groups.

Table 1. Electrospray Mass Spectral Data for Monometallic Complexes of ML^2 and ML^3

Compound	Ions (ESMS) (m/z)[a)]
$[ZnL^2(H^+)_2](PF_6)_2$	$\{[ZnL^2(H^+)_2]^{2+} - H^+\}^+$, (751) $[ZnL^2(H^+)_2]^{2+}$, (376)
$[Co^{III}L^2(H^+)_2](PF_6)_3$	$\{[CoL^2(H^+)_2]^{3+} - 2H^+\}^+$, (745) $\{[CoL^2(H^+)_2]^{3+} - Ph^+\text{-}(H^+)\}^+$, (670) $\{[CoL^2(H^+)_2]^{3+} - Ph^+\}^{2+}$, (336)
$[CoL^3]PF_6$	$[CoL^3]^+$, (749) $\{[CoL^3]^+ - Py\}^+$, (670) $\{[CoL^3]^+ - PhNH^-\}^{2+}$, (329)

a) Most intense peak of isotopic mass distribution.

The resulting monometallic complexes were characterized by elemental analysis, molar conductance, ESMS, ^1H NMR, UV–vis, and IR spectroscopy.

IR Spectra. The infrared spectra of the diimine and diamine monometallic complexes are very similar. Significant differences between the diimines and diamines in the spectra are the emergence of a sharp, but weak, band at about 3370 cm^{-1}, which is attributed to the N–H stretch of the quaternized amine, and the disappearance of a strong band at about 1650 cm^{-1}, corresponding to the C=N stretch of the imine groups.[17]

Electrospray Mass Spectra. Electrospray mass spectrometry is proving to be a very powerful analytical tool for the characterization of macromolecule complexes in the liquid phase, because it allows for the transfer of preexisting ions from solution to the gas phase with minimal fragmentation.[18,19] All major signals for the complexes, including the assignments, are listed in Table 1. Particularly noteworthy is that the presence of a given metal centre is accompanied by a set of signals for each m/z due to the relative isotope abundance. The number and relative intensities of these peaks are unique for each monometallic complex.

Electronic Absorption Spectroscopy. The electronic absorption spectra of the diimine and diamine complexes were

Table 2. Electronic Absorption Maxima and Intensities of the Charge Transfer

Complex	$\lambda_{\max}$ (ϵ, l mol^{-1} cm^{-1})			
$[ZnL^2(H^+)_2](PF_6)_2$	209(16352)	235(25800)	325(18432)	436(14080)
$[Co^{II}L^2(H^+)_2](PF_6)_2$[a)]	196(49100)	235(38240)	320(23632)	444(14496)
$[Co^{III}L^2(H^+)_2](PF_6)_3$		261(48000)	369(22300)	435(7752)[b)]
$[Co^{III}L^3]PF_6$	205(29360)	252(21470)		426(3584)[b)]

a) Spectrum run in deaerated condition. b) Tail into NIR region.

measured in acetonitrile solutions over the range of 190–800 nm. The absorption peaks and their corresponding extinction coefficient are given in Table 2. All of the diimine complexes show an intense absorption band at between about 325 and 369 nm, which is ascribed to the transitions of the azomethine chromophores.[20] The d–d transitions of the Co(II) and Co(III) complexes were not seen, and seemed to be obscured under charge-transfer bands, which was tailed to NIR region.

^{1}H NMR. The ^{1}H NMR spectra of the diamagnetic Zn^{II} and Co^{III} complexes of ligands L^2 and L^3, obtained in CD_3CN solution at 25 °C, confirmed the existence of a single isomer with a C_2 symmetric structure, where the two pyridine ligands are trans disposed. The ^{1}H NMR spectra in CD_3CN reveal broad signals constituting two protons at 15.13 and 15.40 ppm for $[ZnL^2(H^+)_2](PF_6)_2$ and two protons at 15.00 ppm for $[Co^{III}L^2(H^+)_2](PF_6)_3$. These signals are assigned to the protons in the N_2O_2 cavity. These signals were not observed in $[Co^{III}L^3]PF_6$. Upon the addition of a drop of D_2O, rapid proton exchange occurred, and these proton signals disappeared.

Crystal Structure. The X-ray diffraction structure of $[ZnL^2(H^+)_2](PF_6)_2$ was determined. Two views of this cation are shown in Fig. 2, and selected bond distances and angles are given in Table 3. The data collection and refinement parameters are collected in Table 4. Since the molecule has a two-fold symmetry, half of the atoms are numbered, and other half of atoms with identical location properties with the first half are shown with superscripts 2. All bond lengths are unexceptional but certain metal donor atom angles require comment. The Zn donor atom bond lengths (Table 3) are longer to those formed previously for a similar complex,[9] although the Zn–N(1) bonds are slightly shorter. The N(2)–Zn–N(2^2) (the bite angle of the five-membered chelate ring) is rather small (81.7(3)°) and the opposite O(1)–Zn–O(1^2) angle is relatively large (103.3(7)°); they are compressed and broadened, respectively, compared with the analogous Zn complex.[9] The Zn(II) ion is in the six-coordination site and pseudo octahedrally coordinated to two amine nitrogen donors, two phenolic oxygen donors, and two *trans*-pyridine nitrogens; its structure is C_2 symmetric. The absolute configuration about Zn(II) is Δ, Δ, Λ, and the configuration about the nitrogen atoms of the amine group are R, R. The imine groups are tilted 0.681 Å above and below of the plane defined by N(2), N(2^2), O(1), O(1^2); the Zn(II) ion is located in this plane. The open-site cavity defined by two phenolic oxygen atoms and the two imine nitrogen atoms is large. The four potential donor atoms (N(3), N(3^2), O(1), O(1^2)) can not lie in the one plane; the diagonal distances O(1)–N(3^2) and O(1^2)–N(3) are the same (4.493 Å) and too large to accommodate a metal ion of the first transition series. Hydrogen bonding is believed to exist across the O(1) and N(3) and O(1^2) and N(3^2); these distances are identical (2.593 Å).

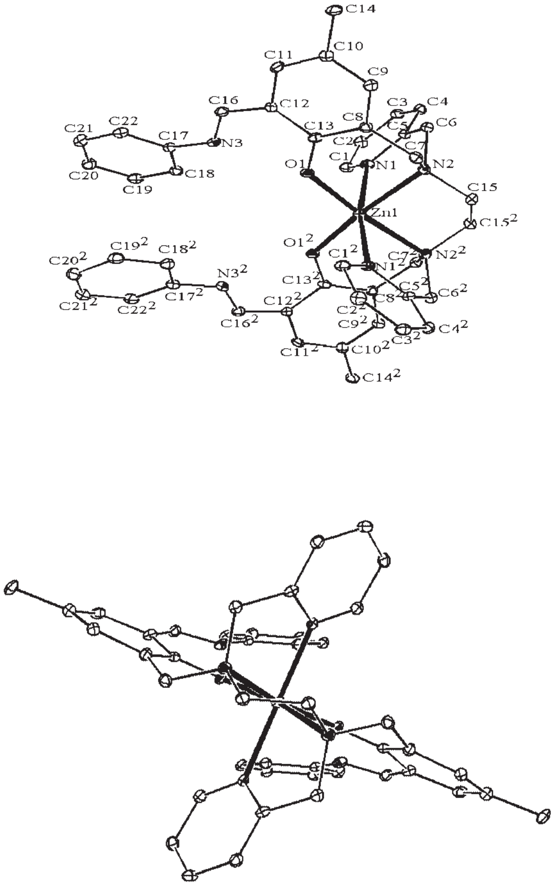


Fig. 2. Two views of the molecular structure of the cation of $[ZnL^2(H^+)_2](PF_6)_2$ drawn with 30% probability ellipsoids. The hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[ZnL^2(H^+)_2]^{2+}$

Bond distances/Å			
Zn–O(1)	2.059 (5)	N(3)–C(16)	1.321 (10)
Zn–N(1)	2.133 (6)	N(3)–C(17)	1.407 (10)
Zn–N(2)	2.241 (6)	N(2)–C(7)	1.476 (10)
Bond angles/deg			
O(1)–Zn–O(1^2)	103.0 (3)	N(2)–Zn–N(2^2)	81.7 (3)
O(1)–Zn–N(2^2)	167.2 (2)	N(1)–Zn–N(1^2)	168.9 (4)
O(1^2)–Zn–N(2^2)	88.1 (2)	N(2)–Zn–O(1^2)	167.2 (2)
O(1)–Zn–N(1)	93.8 (2)	N(1)–Zn–N(2)	79.6 (2)
N(2)–Zn–N(1^2)	92.0 (2)	N(1)–Zn–O(1^2)	93.1 (2)

Table 4. Crystal Data for $[ZnL^2(H^+)_2](PF_6)_2$

Compound	$[ZnL^2(H^+)_2](PF_6)_2$	
Empirical formula	$C_{44}H_{44}F_{12}N_6O_2P_2Zn$	
Formula weight	1044.16	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$C2/c$	
Unit cell dimensions	$a = 10.3420(18)$ Å	$\alpha = 90.000(8)^\circ$
	$b = 31.324(7)$ Å	$\beta = 106.334(6)^\circ$
	$c = 14.163(2)$ Å	$\gamma = 90.000(15)^\circ$
Volume	4402.9(15) Å^3	
Z	4	
Density (calculated)	1.575 mg m^{-3}	
Absorption coefficient	0.728 mm^{-1}	
$F(000)$	2136	
Crystal size	$0.20 \times 0.20 \times 0.15$ mm^3	
Theta range for data collection	1.30 to 24.99°	
Index ranges	$-12 \leqq h \leqq 12, -33 \leqq k \leqq 37, -16 \leqq l \leqq 16$	
Reflections collected	12031	
Independent reflections	3591 [R(int) = 0.1464]	
Completeness to theta = 24.99°	92.5%	
Absorption correction	Semiempirical from equivalents	
Max. and min. transmission	0.8986 and 0.8681	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3591/21/402	
Goodness-of-fit on F^2	1.132	
Final R indices [$I > 2\text{sigma}(I)$]	$R1 = 0.0940$, $wR2 = 0.1404$	
R indices (all data)	$R1 = 0.1850$, $wR2 = 0.1764$	
Extinction coefficient	0.00027(9)	
Largest diff. peak and hole	0.548 and −0.401 e$^-$ Å^3	

Conclusion

This work served to illustrate the preparation and physical propertied of monometallic complexes the binucleating nonmacrocyclic ligands, which are diimine and diamine, and are attached to phenyl groups. The characterization of the prepared complexes demonstrated the presence of two protons in the four-coordination site of the diimine complexes of ML^2, whereas, a lack of protons occurred in the diamine ML^3 complexes. This could be due to more flexibility provided in the amine compounds compared with their imine counterparts which, results in more twisting of the phenyl groups and the amine nitrogens, so that hydrogen bonding might not be achieved between the oxygens of the phenolic groups and the nitrogens of the amines groups. The preparation of the monometallic complexes of ML^3 from two different routes implies that the structures of the complexes are intact even in the present of a labile metal in the six-coordination site. The X-ray crystal structure of ZnL^2 showed that two phenyl groups are tilted above and below the mean molecular plane due to the steric repulsion of two phenyl groups, and is perhaps the major factor for the inability to accommodate the second metal in the N_2O_2 site.

Experimental

Apparatus. Conductance measurements were made at 25 °C with a Jenway 400 conductance meter on 1.00×10^{-3} M samples in CH_3CN. Infrared spectra (potassium bromide disk) were recorded using a Bruker FT-IR instrument; only strong peaks are given. The electronic absorption spectra were measured by using a Cecil 5000 model UV–vis spectrophotometer using spectral-grade CH_3CN. Elemental analyses were performed on a LECO 600 CHN elemental analyzer. Absolute metal percentages were determined by an atomic absorption-flame spectrometer. The ^{1}H NMR spectra were recorded on a Bruker 500 Fourier transform spectrometer. Electrospray mass studies were conducted on a VG Quattro II (Fision) triple-quadruple electrospray mass spectrometer with methanol and as the mobile phase. The compound was dissolved in a mixture of acetonitrile and methanol (1:1), and was injected directly into the spectrometer via a Rheodyne injector using a Fision LC syringe pump to deliver the solution at a flow rate of 20 μL s^{-1}. Nitrogen was used for nebulization and as a drying gas with flow rates of approximately 20 and 250 L h^{-1}, respectively. All samples were dried to constant weight under high vacuum prior to analysis.

Materials. Acetonitrile used was distilled over CaH_2. All preparations of Co(II) complexes were conducted under argon using deaerated solvents. The compounds Li_2L^1,[7] $Co^{II}L^1$, $[Co^{III}L^1]PF_6$, and ZnL^1[10] were prepared by standard methods found in the literature.

$[ZnL^2(H^+)_2](PF_6)_2$. To a stirred suspension of ZnL^1 (0.5 g, 0.81 mmol) in methanol (20 mL) was added dropwise over 1 h a solution of aniline (150 μL, 1.62 mmol) and acetic acid (95 μL, 1.66 mmol) in ethanol (10 mL). After the addition was completed, all starting materials were dissolved. The yellow solution was stirred for 3 h. A yellow solid precipitated almost immediately after the addition of a filtered solution of NH_4PF_6 (0.37 g, 2.30

mmol) in ethanol (10 mL). The solid was collected and was washed with ethanol (2 × 10 mL), Et_2O (2 × 10 mL), hexane (2 × 10 mL). The crude compound was recrystallized, which yielded $[ZnL^2(H^+)_2](PF_6)_2$ as yellow needles (77%). A crystal suitable for X-ray crystal structure determination was grown by vapor diffusion of ethanol into a CH_3CN: ethanol solution of the complex. $\Lambda_m = 273\ \Omega^{-1}\,mol^{-1}\,cm^2$. Anal. Found: C, 50.43; H, 4.08; N, 8.26; Zn, 6.33%. Calcd for $C_{44}H_{44}N_6O_2P_2F_{12}Zn$: C, 50.61; H, 4.25; N, 8.05; Zn, 6.26%. FT-IR (KBr disk) 1645 (C=N), 2940 (N–CH_2), 1450 (aromatic skeleton) cm^{-1}. ^1H NMR (500.13 MHz, CD_3CN): δ 2.26 (s, 6H), 3.05, 3.15 (sys AB, $J_{AB} = 10.3$ Hz, 4H), 3.60 (d, $J = 13.0$ Hz, 2H), 4.10–4.40 (m, 6H), 7.00–7.50 (m, 20H), 7.82 (t, $J = 7.9$ Hz, 2H), 8.63 (d, $J = 10.4$ Hz, 1H), 8.79 (d, $J = 5.1$ Hz 1H), 15.13 (br s, 1H), 15.40 (br s, 1H).

$[CoL^2(H^+)_2](PF_6)_2$. This compound was prepared by the general procedure described for $[ZnL^2(H^+)_2](PF_6)_2$. Fine orange needles were obtained after recrystallization (90%). $\Lambda_m = 283\ \Omega^{-1}\,mol^{-1}\,cm^2$ (taken under deaerated condition). Anal. Found: C, 50.67; H, 4.48; N, 8.26; Co, 5.51%. Calcd for $C_{44}H_{44}N_6O_2P_2F_{12}Co$: C, 50.93; H, 4.27; N, 8.10; Co, 5.68%. FT-IR (KBr disk) 1650 (C=N), 2942 (N–CH_2), 1447 (aromatic skeleton) cm^{-1}.

$[Co^{III}L^2(H^+)_2](PF_6)_3$. Method 1: To a stirred solution of the $[CoL^2(H^+)_2](PF_6)_2$ (0.25 g, 0.24 mmol) in deaerated CH_3CN (5 mL) under argon was added $[Cp_2Fe]PF_6$ (0.80 g, 0.24 mmol) in deaerated CH_3CN (5 mL). The resultant dark solution was stirred under argon for 30 min, and was then opened to the air and concentrated to dryness. The residue was triturated with Et_2O (3 × 5 mL) in order to remove Cp_2Fe. The residue was collected, washed with ethanol (2 × 5 mL), Et_2O (2 × 5 mL), and hexane (2 × 5 mL) and dried under a vacuum. The dark solid was recrystallized, which yielded 90%. $\Lambda_m = 378\ \Omega^{-1}\,mol^{-1}\,cm^2$. Anal. Found: C, 44.32; H, 3.77; N, 7.39; Co, 4.80%. Calcd for $C_{44}H_{44}N_6O_2P_3F_{18}Co$: C, 44.68; H, 3.75; N, 7.11; Co, 4.98%. FT-IR (KBr) 1642 (C=N), 2943 (N–CH_2), 1452 (aromatic skeleton) cm^{-1}. ^1H NMR (500.13 MHz, CD_3CN): δ 2.35 (s, 6H), 3.12 (m, 2H), 3.50–4.00 (m, 6H), 4.50–5.00 (m, 4H), 7.00–8.10 (m, 20H), 9.05 (m, 2H), 10.04 (s, 2H), 15.00 (br s, 2H). When one drop of D_2O was added to the ^1H NMR sample, the broad signal at 15.00 ppm disappeared.

Method 2: To a stirred solution of $[Co^{III}L^1]PF_6$ (0.30 g, 0.5 mmol) in CH_3CN (10 mL) was added dropwise over 1 h a solution of aniline (92 µL, 1 mmol) and acetic acid (115 µL, 2 mmol) in ethanol (10 mL). The dark solution was stirred for 3 h. A filtered solution of NH_4PF_6 (0.08 g, 0.5 mmol) in ethanol (2 mL) then added to the solution, and the resultant dark solution was taken to dryness. The residue was collected, washed with ethanol (2 × 5 mL), Et_2O (2 × 5 mL), and hexane (2 × 5 mL) and dried under a vacuum. The yield of the reaction after purification was 60%. Anal. Found: C, 44.54; H, 3.99; N, 7.21; Co, 4.82%. Calcd for $C_{44}H_{44}N_6O_2P_3F_{18}Co$: C, 44.68; H, 3.75; N, 7.11; Co, 4.98%. The identity of the compound obtained was confirmed by ^1H NMR, UV–vis, and IR spectra, whose characteristics compared well with those prepared by method 1.

Preparation Amine Complexes. The amine complexes are air stable as solids. These complexes were purified by recrystallization from CH_3CN–C_2H_5OH by the same procedure as described for the imine complexes.

$Co^{II}L^3$. To a stirred solution of $[CoL^2(H^+)_2](PF_6)_2$ (0.30 g, 0.29 mmol) in CH_3CN (10 mL) under a argon atmosphere and at 0 °C was added dropwise over 15 min a solution of $NaBH_4$ (0.22 g, 0.58 mmol) in deaerated ethanol (5 mL). A light-brown solid precipitated almost immediately. After precipitation was completed deaerated acetic acid (342.4 µL, 6 mmol) was added to the reaction mixture, which produced a small amount of gas evolution. The solid was then collected and washed with water (3 × 5 mL), ethanol (3 × 5 mL), Et_2O (3 × 5 mL), and hexane (2 × 5 mL), and dried under high a vacuum (54%). The resulting product was stable as a solid in air. Anal. Found: C, 70.12; H, 6.20; N, 11.48; Co, 7.56%. Calcd for $C_{44}H_{46}N_6O_2Co$: C, 70.48; H, 6.18; N, 11.21; Co, 7.68%. FT-IR (KBr disk) 1604 (N–H bend), 2938 (N–CH_2), 1451 (aromatic skeleton), 3368 (N–H stretch) cm^{-1}.

$[Co^{III}L^3]PF_6$. Methode 1: To a stirred solution of $[Co^{III}L^2(H^+)_2](PF_6)_3$ (0.5 g, 0.423 mmol) in CH_3CN (10 mL) at 0 °C was added dropwise over 15 min a solution of $NaBH_4$ (0.32 g, 0.85 mmol) in deaerated ethanol (10 mL). The resultant dark solution was stirred for 30 min at 0 °C, and was then warmed to 25 °C over 15 min. Acetic acid (342.4 µL, 6 mmol) was added to the reaction mixture and a small amount of gas evolution was observed. The solution was heated to 90 °C and water (5 mL) was added. The solvents were slowly distilled off over 30 min until a dark solid precipitated. After cooling the suspension to room temperature, the solid was collected, washed with warm water (3 × 5 mL), ethanol (3 × 5 mL), Et_2O (3 × 5 mL), and hexane (2 × 5 mL), and dried under vacuum. The crude product was recrystallized (60%). $\Lambda_m = 151\ \Omega^{-1}\,mol^{-1}\,cm^2$. Anal. Found: C, 58.79; H, 5.02; N, 9.55; Co, 6.44%. Calcd for $C_{44}H_{46}N_6O_2PF_6Co$: C, 59.06; H, 5.18; N, 9.39; Co, 6.59%. FT-IR (KBr) 1602 (N–H bend), 2940 (N–CH_2), 1455 (aromatic skeleton), 3360 (N–H stretch) cm^{-1}. ^1H NMR (500.13 MHz, CD_3CN) δ 2.79 (s, 6H), 3.00–5.00 (m, 16H), 5.07 (m, 2H), 6.00–8.20 (m, 22H).

Method 2: To a stirred suspension of the $Co^{II}L^3$ (0.20 g, 0.27 mmol) in deaerated CH_3CN (5 mL) under argon was added $[Cp_2Fe]PF_6$ (0.72 g, 0.27 mmol) in deaerated CH_3CN (5 mL). The initial light-brown suspension slowly turned black upon the addition of $[Cp_2Fe]PF_6$. The reaction mixture was stirred for 1 h, and was then filtered through Celite. The filtrate was concentrated to dryness. The product was triturated with Et_2O (3 × 10 mL) in order to remove Cp_2Fe. The residue was collected and washed with ethanol (2 × 3 mL), Et_2O (3 × 5 mL), and hexane (2 × 5 mL), and dried under a vacuum. The crude product was recrystallized (47%). Anal. Found: C, 59.37; H, 4.93; N, 9.35; Co, 6.70%. Calcd for $C_{44}H_{46}N_6O_2PF_6Co$: C, 59.06; H, 5.18; N, 9.39; Co, 6.59%. The identity of the obtained compound was confirmed by ^1H NMR, UV–vis, and IR spectra, whose characteristics compared well with those prepared by method 1.

ZnL^3. This compound was prepared by the method used to prepare $Co^{II}L^3$. ZnL^3 was obtained as a white solid (59%). This compound was almost insoluble in common solvents. Anal. Found: C, 69.98; H, 5.81; N, 11.02; Zn, 8.60%. Calcd for $C_{44}H_{46}N_6O_2Zn$: C, 69.88; H, 6.13; N, 11.11; Zn, 8.65%. FT-IR (KBr disk) 1610 (N–H bend), 2943 (N–CH_2), 1452 (aromatic skeleton), 3370 (N–H stretch) cm^{-1}.

Crystallographic Structural Determination. The single-crystal X-ray diffraction structure of $[ZnL^2(H^+)_2](PF_6)_2$ was determined at 150(2) K. The crystallographic data are summarized in Table 4. The data were measured on a Nonius Kappa CCD diffractometer using graphite-monochromated radiation. The structure was solved by direct methods using SHELXS, and subjected to full-matrix leastsquares using SHELXL. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were subjected to isotropic refinement. The zinc atom was located on a crystallographic two-fold axis, so that the asymmetric unit only contained half of the ligand system, and other half was generated by a symmetry operation. One of the PF_6 anions was disordered and some of its fluorine atoms were distributed over two, semipopulated sites.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-CCDC 262374 for compound ZnL^3. Copies of the data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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