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[(Tmp)Co_2L] Complexes through Preassembly on 2,6-Diformyl- and 2,6-Bis(benzylimino)-4-methylphenolate Templates

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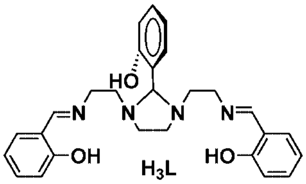
The reaction of the dinucleating ligand H_3L {2-(2′-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine} with $Co(OAc)_2{\cdot}4H_2O$ and NaN_3 in MeOH produces the methoxide-bridged dicobalt complex $[Co^{III}_2(\mu\text{-}OMe)L(N_3)_2]$ (**1**) under aerobic conditions. If the reaction occurs in the presence of either 2,6-diformyl-4-methylphenolate (dfp^-) or 2,6-bis(benzyliminomethyl)-4-methylphenolate (bip^-), a preassembly of the $[Co^{II}_2(OPh)]^{3+}$ units takes place on these templates before coordination with L^{3-} in $[Co^{II}_2(\mu\text{-}dfp)L]{\cdot}3H_2O$ (**2**·$3H_2O$) and $[Co^{II}_2(\mu\text{-}bip)L]{\cdot}3H_2O$ (**3**·$3H_2O$), respectively. Incorporation of these coligands into the structure leads to stabilization of 3+ and 2+ oxidation states of the cobalt. In complex **2**, the Co^{II} ions are engaged in a weak antiferromagnetic interaction.

Introduction

Dinuclear high-spin cobalt(II) complexes have been the subject of recent investigations in molecular magnetism and magnetic analysis.[1] These high-spin cobalt(II) complexes show interesting magnetic properties, where the ground term possesses an orbital angular moment.[2] Cobalt can also give rise to mixed-valent complexes because of its ready access to 2+ and 3+ oxidation states. These complexes have attracted attention because of their fascinating magnetic properties as well as their biological relevance. They can serve as synthetic models of dimetallic biosites, such as in methionine aminopeptidase,[3] and can show DNA cleavage activity.[4] This type of metallohydrolase is known to require two or more metal ions for hydrolysis of phosphate ester and peptide bonds.[5] Recently, Love and co-workers have used a binucleating macrocycle to prepare low-spin square-planar $Co^{II}Co^{II}$ diporphyrin complexes having a pacman-like cleft showing interesting dioxygen reduction chemistry.[6] Because of these various interesting features of cobalt ions, we studied their reactivity toward imidazolidinyl ligands.[7] We and others have been exploring the dinucleating properties of the ligand H_3L (Scheme 1) {2-(2′-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine}[8] and its close derivative H_3L' {2-(2′-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-4-methyl-3-azabut-3-enyl]-2-methyl-1,3-imidazolidine}[9] for various reasons, including their importance in coordination chemistry, molecular magnetism, and catalysis.[9–16]



Scheme 1.

During the course of these investigations, we have observed that in certain conditions, complexation reactions with Mn^{III}, Fe^{III}, Co^{III}, or Cu^{II} led to the hydrolysis of the imidazolidine ring[17,18] and even the destruction of one of the imine linkages of the hexadentate proligand.[19] We have also investigated the hydrolysis of H_3L as triggered by Co^{III} and isolated the mononuclear complex resulting from the hydrolyzed ligand.[7] Previously Fondo et al. showed that this type of ligand leads to either Co^{III}_2 or mixed-valent $Co^{III}Co^{II}$ complexes[20] by spontaneous oxidation of Co^{II} salts in air. The main objectives of the present investigation are (i) to scrutinize the role of the different ligand templates in inhibition of the coordination-induced hydrolysis of the imidazolidine ring of the trisphenolate ligands, (ii) to synthesize a new Co_2 complex of this ligand incorporating template ligands, and (iii) to stabilize the 2+ oxidation states of cobalt in phenolate environments. We have successfully achieved our goal by using 2,6-diformyl-4-methylphenol (Hdfp) and 2,6-bis(benzyliminomethyl)-4-methylphenol (Hbip) as coligands (Scheme 2).

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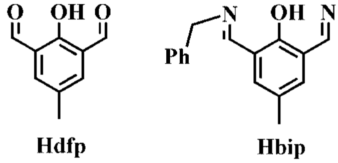


Scheme 2.

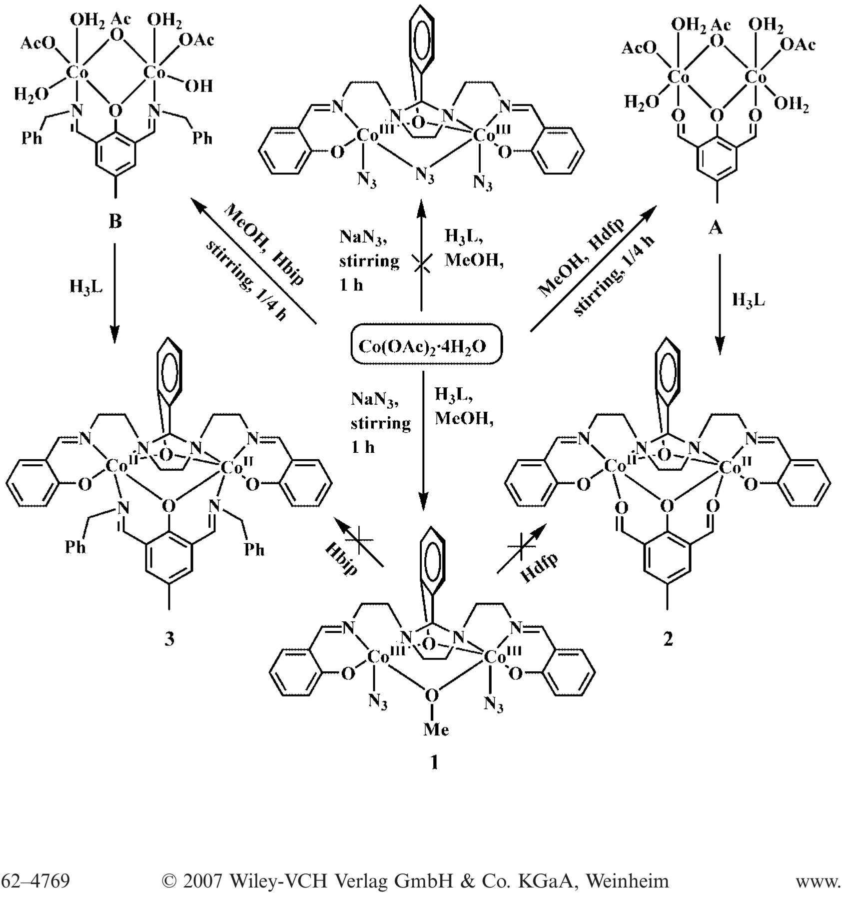
These coligands not only inhibit hydrolysis of L^{3-} but also serve as templates to stabilize the metal ions in 2+ oxidation states in two new $[Co_2]$ complexes. Hydroxy carboxaldehydes of this type have been used extensively as precursors in the preparation of more complicated ligands,[21] however their use as exogenous bridging ligands is very uncommon.[22] While exploring the metal ion coordination processes toward L^{3-}, we found that the reactions of a particular metal salt control the production of the desired complex in the presence and absence of externally added or solvent-derived template bridges. Herein complexes $[Co^{III}_2(\mu\text{-}OMe)L(N_3)_2]$ (**1**), $[Co^{II}_2(\mu\text{-dfp})L]\cdot 3H_2O$ (**2**$\cdot 3H_2O$), and $[Co^{II}_2(\mu\text{-bip})L]\cdot 3H_2O$ (**3**$\cdot 3H_2O$) derived from ligand H_3L following two different (solvent-derived or external) template routes are reported. Complexes **1** and **2**$\cdot 3H_2O$ were crystallographically characterized and the magnetic properties of **2**$\cdot 3H_2O$ were also studied.

Results and Discussion

Syntheses, Reactivity, and Spectroscopic Characterizations

The ligand H_3L {2-(2′-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine} (Scheme 1) was prepared according to a literature procedure[8] and its reaction with cobalt(II) salts has been investigated, as shown in Scheme 3.

In MeOH, the reaction of $Co(OAc)_2\cdot 4H_2O$ and NaN_3 followed by addition of a methanolic solution of H_3L in a 2:2:1 molar ratio yields brown $[Co^{III}_2(\mu\text{-}OMe)L(N_3)_2]$ (**1**) in 75% yield while stirring in air at room temperature (300 K). Complex **1** could be isolated in high purity and shows aerial oxidation of metal centers. It has also been observed that use of excess NaN_3 up to a molar ratio of 1:6 could not substitute the bridging MeO^- group by N_3^- and afforded **1** exclusively. In a previous report, we noticed that in solution H_3L is unstable during reactions with cobalt(II) salts and produced crystals of the mononuclear complex cations $[CoL']^+$ in low yield (H_2L' is the hexadentate proligand formed from the imidazolidine ring hydrolysis of H_3L).[7] As an *o*-formylphenolate moiety is generated from the hydrolysis of L^{3-}, which indicates that the ligand decomposition is possibly inhibited by this. Therefore the solution stability of L^{3-} as part of new $[Co_2]$ complexes could be enhanced with the introduction of diformyl- and bis(benzylimino)phenolates as template ligands. 2,6-Diformyl-4-meth-



Scheme 3.

ylphenol (Hdfp)[21] and 2,6-bis(benzyliminomethyl)-4-methylphenol (Hbip)[23] have been synthesized following the methods previously described and satisfactorily characterized by elemental analysis, IR, and ^{1}H NMR spectroscopy. Binucleating ligands based on this dialdehyde as introduced by Robson[24] and Okawa[25] have been extensively studied for the preparation of different dimetal complexes. The process of ligand hydrolysis, however, was inhibited completely if Hdfp or Hbip had previously been mixed with the solution of $Co(OAc)_2{\cdot}4H_2O$. Presumably this led to the formation of intermediate **A** or **B** (Scheme 3), to result in the formation of complexes **2** and **3**, after addition of H_3L where the deprotonated dicarbonyl phenolate (dfp^-) and bis(benzylimino)phenolate (bip^-) behave as bisdidentate bridging ligands stabilizing the Co^{II}_2 complexes. The formulation of all the complexes is consistent with the elemental and metal analysis, and solution electrical conductivity data in CH_3CN. The red complex **2** forms in 80% yield whilst stirring in MeOH at 300 K. Similarly, compound **3** was isolated in 75% yield as a red powder. All the compounds are insoluble in water and separate directly from the reaction mixture following the completion of the reactions in air at room temperature. Stabilization of the metal oxidation states within these Co_2 complexes is template-ligand-dependent. Template interconversions within this family of the complexes are not possible in the presence of external oxidizing and reducing agents. This clearly identifies that the templates are present as an integral part within these assemblies.

Infrared Spectroscopy

The sharp peak in the FTIR spectra of complexes **1**, **2**$\cdot 3H_2O$, and **3**$\cdot 3H_2O$, at 1629, 1625, and 1624 cm^{-1} respectively, are characteristic of the C=N functionality of the ligand L^{3-}. The C=N stretching frequency of the free Hbip ligand is shifted from 1636 cm^{-1} to 1601 cm^{-1} in **3**$\cdot 3H_2O$. Broad medium bands at 3396 and 3422 cm^{-1} are observed corresponding to ν(OH) vibrations from lattice water molecules in complexes **2**$\cdot 3H_2O$ and **3**$\cdot 3H_2O$, respectively. In addition, complex **1** shows a very strong sharp band at 2025 cm^{-1} for the $\nu_{as}(N_3^-)$ stretching[26] and the $\nu_s(N_3^-)$ appears at 1322 cm^{-1}. The position of this band is consistent with terminal azide coordinations, as observed in other cobalt(III) complexes.[27] Complex **2** also shows a sharp band at 1597 cm^{-1} due to the coordinated ν(C=O) functionality of the dfp^- ligand.

Electronic Spectroscopy

In MeCN solution, the brown compound **1** shows a band at 639 nm (ε = 470 L mol^{-1} cm^{-1}) and is characteristic of the octahedral cobalt(III) environment ($^1A_{1g} \rightarrow {}^1T_{1g}$) in the d–d spectra. The charge transfer transitions ($L \rightarrow Co^{III}$ and intraligand) occur at 349 nm (ε = 4600 L mol^{-1} cm^{-1}) and 271 nm (7600 L mol^{-1} cm^{-1}) with an overlapping contribution of $^1A_{1g} \rightarrow {}^1T_{2g}$ in the former. Complex **2** shows d–d transition at 562 nm (ε = 310 L mol^{-1} cm^{-1}) and charge transfer transitions at 375 and 271 nm with molar extinction coefficients of 2400 and 12500 L mol^{-1} cm^{-1}. Similarly, complex **3** shows d–d transition at 591 nm (ε = 361 L mol^{-1} cm^{-1}) and charge transfer transitions at 401 (2100 L mol^{-1} cm^{-1}) and 274 nm (8700 L mol^{-1} cm^{-1}). In a reported octahedral Co^{II} compound, observation of the three bands around 450, 550, and 850 nm are assigned to spin-allowed excitations from the $^4T_{1g}$(F) ground state.[28] So for compounds **2** and **3** the bands at 562 and 591 nm may be assigned to the spin-allowed transitions from $^4T_{1g}$(F) to $^4A_{2g}$.

The Role of Template Anions in the Stabilization of the Ligand Imidazolidine Ring

Earlier we showed that expulsion of 1 mol of 2-hydroxybenzaldehyde molecules takes place when cobalt ions react with the ligand H_3L in aqueous MeOH solution in air, which is different from the selective imidazolidine ring-opening reaction for a different ligand system with no loss of aldehyde molecule.[29] In the presence of solvent-generated MeO^- template and terminal N_3^- coordination, a similar situation did not arise leading to imidazolidine ring hydrolysis. Thus the presence of both MeO^- and N_3^- stabilizes the imidazolidine ring and cobalt ions in 3+ oxidation states. Also terminal double N_3^- coordination did not provide any tetranucleation through *cis*-1,3-N_3^- bridges. In exactly the same fashion 2,6-diformyl- and 2,6-bis(benzylimino)-4-methylphenolate templates (Tmp) stabilize the L^{3-} against imidazolidine ring hydrolysis and 2+ oxidation states of cobalt ions in a new family of Co_2 complexes. The nature of the final reaction product is greatly influenced by the ligands used in different steps, the solvent system, and the sequence of addition of reactants.

X-ray Crystallographic Procedures for 1 and 2·3H₂O

The intensity data of complexes **1** and **2** were collected on a Nonius CAD4 X-ray diffractometer using single-crystal graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) by the ω-scan method. Data were collected at 293 K. Information concerning X-ray data collection and structure refinement of the compound is summarized in Table 1. For complex **1**, a total of 4926 reflections were recorded with Miller indices $h_{min} = -11$, $h_{max} = 0$, $k_{min} = 0$, $k_{max} = 24$, $l_{min} = -16$, and $l_{max} = 16$. For complex **2**, a total of 6861 reflections were recorded with Miller indices $h_{min} = 0$, $h_{max} = 23$, $k_{min} = 0$, $k_{max} = 23$, $l_{min} = 0$, and $l_{max} = 21$. In the final cycles of full-matrix least-squares on F^2 all non-hydrogen atoms were assigned anisotropic thermal parameters. The positions of the H atoms bonded to C atoms were added (C–H distance 0.97 Å) in the riding model. The structure was solved using the SHELX-97[30] program system.

Table 1. Crystallographic data for **1** and **2**·3H_2O.

	1	**2**·3H_2O
Empirical formula	$C_{28}H_{30}Co_2N_{10}O_4$	$C_{36}H_{39}Co_2N_4O_9$
Formula mass	688.477	896.63
Crystal system	monoclinic	tetragonal
Space group	$P2_1/c$	$P42_1c$
a [Å]	9.749 (2)	19.8524(10)
b [Å]	21.000(10)	19.8524(10)
c [Å]	14.155(3)	18.499(2)
β [°]	96.96(2)	
D_{calcd} [g cm^{-3}]	1.590	1.429
Z	2	8
$F(000)$	1416	3231
Crystal size [mm]	0.26 × 0.18 × 0.16	0.34 × 0.28 × 0.24
μ [mm^{-1}]	1.208	0.968
θ range [°]	1.74–24.99	1.45–24.98
R_1[a], wR_2 [$I > 2\sigma(I)$]	0.1030, 0.2289	0.0588, 0.1410
Gof on F^2	0.933	1.048
Final difference map Max., min. [e Å^{-3}]	0.849, –1.528	0.633, –0.375

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$. $w = 0.75/[\sigma^2(F_o) + 0.0010F_o^2]$.

Description of Structures

Single crystals suitable for X-ray structure determinations were obtained by slow evaporation of a MeOH/CH_3CN (1:1) solution of **1** and a MeOH solution of **2**·3H_2O after a week. The atom labeling scheme and molecular views (ORTEP) of the complexes are shown in Figures 1, 2, 3, and 4. Selected interatomic distances and angles are collected in Tables 2 and 3.

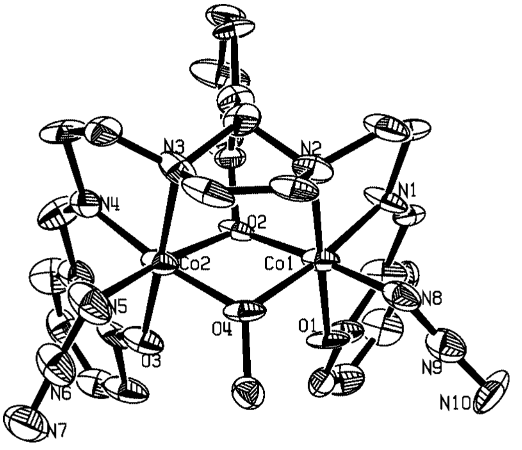


Figure 1. ORTEP representation of $[Co^{III}_2(\mu\text{-OMe})L(N_3)_2]$ (**1**) at the 40% probability level. Hydrogen atoms are omitted for clarity. Only independent non-carbon atoms are labeled.

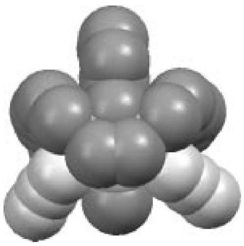


Figure 2. The ψ-like shape of the ligand covers the Co(μ-OMe)Co unit of **1** in a space-filling model when viewed along one intermediate axis (deep grey: ligand carbon; light grey: nitrogen).

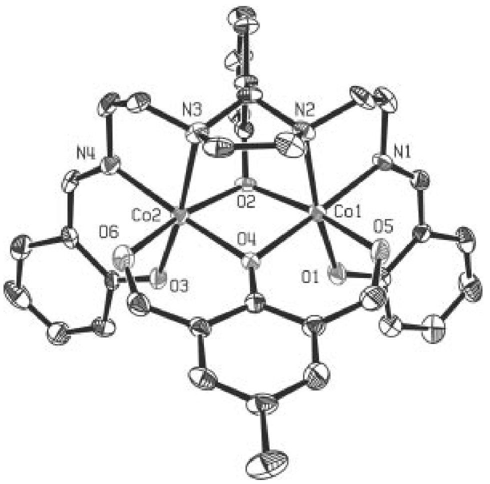


Figure 3. ORTEP representation of $[Co_2(\mu\text{-dfp})L]$ (**2**) at the 30% probability level. Hydrogen atoms are omitted for clarity. Only independent non-carbon atoms are labeled.

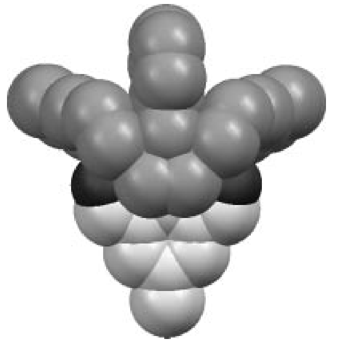


Figure 4. The template ligand in an "ice-cream cone" shape holds the Co(μ-OPh)Co unit in a space-filling model when viewed along one intermediate axis (light grey: template carbon; dark grey: ligand carbon; black: oxygen).

$[Co^{III}_2(\mu\text{-OMe})L(N_3)_2]$ (1)

Complex **1** (Figure 1) is a neutral aggregate of two Co^{III} ions linked by the template action of solvent-derived MeO^- and capping coordination of the heptadentate ligand L^{3-}.

The unit cell of **1** consists of $[Co^{III}_2(L)(\mu\text{-OMe})(N_3)_2]$ neutral molecules, without any solvent of crystallization. Each tetradentate N_2O_2 pocket binds Co^{III} ions in *cis* fashion; *facial* coordination involves bridging phenolate O, imidazolidine, and imine N atoms. The bridging function is accomplished by the central imidazolidine group (NCN group) and phenolate moiety (one μ-O) of L^{3-}, while the imine N-atom and the phenoxide O-donor at each side of the ligand saturate two additional coordination sites of each Co^{III} center. The MeO^- group, in preference to the N_3^- group, contributes to the bridging within the complex and functions as a template in the absence of any externally added chelating exogenous template ligand. Hexacoordina-

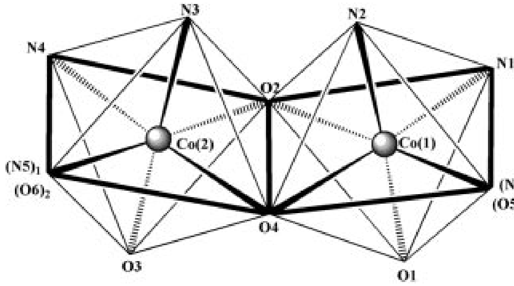
Table 2. Selected interatomic distances [Å] and angles [°] for complex **1**.

Co1–O1	1.867(8)	N5–Co2–O2	172.3(6)
Co1–N1	1.871(11)	O3–Co2–N3	178.2(6)
Co1–N8	1.883(15)	O4–Co2–N3	89.5(5)
Co1–O4	1.894(9)	N4–Co2–N3	84.8(6)
Co1–O2	1.899(10)	N5–Co2–N3	88.3(5)
Co1–N2	2.031(11)	O2–Co2–N3	91.8(4)
Co2–O3	1.851(9)	O1–Co1–N1	95.5(4)
Co2–O4	1.875(11)	O1–Co1–N8	92.3(5)
Co2–N4	1.879(15)	N1–Co1–N8	90.9(5)
Co2–N5	1.930(13)	O1–Co1–O4	90.7(4)
Co2–O2	1.955(9)	N1–Co1–O4	172.5(5)
Co2–N3	2.032(11)	N8–Co1–O4	93.1(5)
Co2···Co1	2.869(3)	O1–Co1–O2	87.6(4)
		N1–Co1–O2	94.6(5)
O3–Co2–O4	92.2(4)	N8–Co1–O2	174.4(5)
O3–Co2–N4	93.4(5)	O4–Co1–O2	81.4(4)
O4–Co2–N4	172.3(5)	O1–Co1–N2	179.0(5)
O3–Co2–N5	92.3(5)	N1–Co1–N2	85.1(5)
O4–Co2–N5	91.9(6)	N8–Co1–N2	86.9(5)
N4–Co2–N5	93.0(6)	O4–Co1–N2	88.8(4)
O3–Co2–O2	87.9(4)	O2–Co1–N2	93.2(4)
O4–Co2–O2	80.4(4)	Co1–O2–Co2	96.2(4)
N4–Co2–O2	94.6(5)	Co2–O4–Co1	

Table 3. Selected interatomic distances [Å] and angles [°] for complex **2**.

Co1–O1	1.960(9)	O4–Co2–O6	84.7(4)
Co1–N1	2.019(10)	O3–Co2–N3	173.0(4)
Co1–O2	2.050(9)	N4–Co2–N3	81.6(5)
Co1–O4	2.085(8)	O2–Co2–N3	87.1(3)
Co1–O5	2.103(9)	O4–Co2–N3	90.0(4)
Co1–N2	2.254(11)	O6–Co2–N3	90.8(4)
Co2–O3	1.998(9)	O1–Co1–N1	90.0(4)
Co2–N4	2.026(12)	O1–Co1–O2	94.5(3)
Co2–O2	2.051(7)	N1–Co1–O2	102.7(4)
Co2–O4	2.057(8)	O1–Co1–O4	97.4(3)
Co2–O6	2.144(9)	N1–Co1–O4	170.9(4)
Co2–N3	2.261(10)	O2–Co1–O4	82.0(3)
		O1–Co1–O5	89.8(4)
O3–Co2–N4	91.4(4)	N1–Co1–O5	89.6(4)
O3–Co2–O2	93.7(3)	O2–Co1–O5	167.0(3)
N4–Co2–O2	102.1(4)	O4–Co1–O5	85.2(3)
O3–Co2–O4	96.9(4)	O1–Co1–N2	172.2(4)
N4–Co2–O4	170.1(4)	N1–Co1–N2	82.2(4)
O2–Co2–O4	82.7(3)	O2–Co1–N2	87.0(3)
O3–Co2–O6	89.9(4)	O4–Co1–N2	90.4(4)
N4–Co2–O6	90.1(4)	O5–Co1–N2	90.5(4)
O2–Co2–O6	167.2(4)	Co2–O4–Co1	95.8(4)
		Co1–O2–Co2	97.0(3)

tion around each Co ion is achieved through terminal binding of two N_3^- ions. Each Co atom is thus coordinated in a distorted octahedral N_3O_3 environment in which the two octahedra sharing the edge are defined by the bridging phenolate and methoxide O atoms (Scheme 4 with N5 and N8). The planes intersecting at this edge form an angle of 162.95°, as a result of the folding imposed by the imidazolidine ring [N2···N3 distance of 2.342(4) Å]. The geometric restrictions resulting from L^{3-} also cause the Co–O–Co angles to be different [96.2(4)° and 99.1(4)°] for endogenous phenolate and exogenous methoxide oxygen atoms, respectively. The sums of the angles around the oxygen atoms of the central phenolate and methoxide bridges are 330.37° and 342.03° and demonstrate that the pyramidal distortion is more pronounced in the case of phenolate O atom because of a folding of the ligand L^{3-} around the imidazolidine backbone. The intramolecular Co···Co distance is 2.869(3) Å. The O–Co–O angles [81.4(4)° and 80.4(4)°] within the metallacyclic $Co_2(\mu\text{-}O)_2$ diamond core indicate distortions at the metal ion octahedra. The degree of distortion from an ideal octahedral (90°) geometry is reflected in the *cisoid* [95.4(4)–80.4(4)°] and the *transoid* [179.0(5)–172.3(5)°] angles. The bridging Co–O(phenolate) distances [1.955(9) Å] are longer than the terminal distances (av. 1.859 Å).



Scheme 4.

The Co–N(imidazolidine) [2.031(11) and 2.032(11) Å] and Co–N(imine) [1.871(11) and 1.879(15) Å] distances are clearly different. The terminal Co–N(azide) distances [1.883(15) and 1.930(13) Å] are intermediate between the above two distances.[31] The azide terminals are almost linear, with N–N–N angles 172.6(19)–172.8(17)°. The nonlinear monodentate coordination of N_3^- is reflected in the Co–N–N angles of 121.0(11) and 118.0(10)°. Perfect covering of the Co(μ-OMe)Co unit by a ψ-like appearance of the ligand in a space-filling model is shown in Figure 2.

In crystal packing no H-bonding network is present because of the absence of solvate molecules within the crystal lattice. The crystal-packing diagram is shown in Figure S1 (see Supporting Information).

[Co^{II}_2(μ-dfp)L]·$3H_2O$ (2·$3H_2O$)

The unit cell of **2**·$3H_2O$ consists of a dinuclear complex [Co_2(μ-dfp)L] (**2**) (Figure 3) along with three water molecules. Complex **2** is a neutral aggregate of Co^{II} ions bridged and chelated by the ligand L^{3-} in the same manner as in complex **1**. The bridging and hexacoordination of both metals is completed by a symmetric 2,6-diformylphenolate (dfp$^-$) ligand that terminally binds both metals through each of its carbonyl groups, while linking them through the central phenolate μ-O. This type of exogenous bridging coordination mode of the 2,6-diformyl-4-methylphenolate anion is quite unusual. The bridging bisdidentate ligand dfp$^-$ naturally binds the edges offered by the [$Co_2L]^+$ moiety (Scheme 4), therefore the exchange of two N_3^- and MeO^- ions for dfp$^-$ in going from **1** to **2** does not introduce significant changes to the overall metric parameters of the complex. Each Co atom is thus coordinated in a distorted octahedral N_2O_4 environment in which the two octahedra sharing the edge are defined by the bridging phenolate oxygen atoms of different origin (Scheme 4 with O5 and O6). The planes intersecting at this edge form an angle of 160.94° as a result of the folding imposed by the imidazolidine ring (N2···N3 distance of 2.303 Å). The geometric restrictions resulting from L^{3-} also cause the Co–O–Co angles to be different [97.0(3)° and 95.8(4)°] for endogenous and exogenous phenolate O atoms, respectively. The sums of the angles around the oxygen atoms of the central endogenous and exogenous phenolates are 333.28° and 359.16°, indicating the pyramidal and planar nature of phenolate oxygen atoms of different origin. The Co···Co separation at 3.073 Å is longer than 2.869(3) Å in **1** and is due to the different oxidation levels of cobalt ions in octahedral geometries. The O–Co–O angles [82.0(3) and 82.7(3)] within the metallacyclic $Co_2(\mu\text{-}O)_2$ diamond core indicate distortions at the metal ion octahedra.

The degrees of distortion from an ideal octahedral (90°) geometry are reflected in the *cisoid* [102.7(4)–82.0(3)°] and the *transoid* [173.0(4)–167.0(3)°] angles. Compared to Cu_2 binding[9,19] in *meridional* mode with apical AcO^- or N_3^- bridging, the dfp^- template in the present case forces a *facial* binding [chelate bite angles are 102.7(4), 87.0(3), and 82.2(4)° around Co1 and 102.1(4), 87.1(3), and 81.6(5)° around Co2] of the O(central phenolate)N(imidazolidine)-N(imine) part of L^{3-}.

Earlier we showed that in Cu_2 complexes each tetradentate N_2O_2 pocket endorses either square-pyramidal or distorted trigonal-bipyramidal geometry. Now we report its potential to accommodate Co^{II} ions in octahedral geometries that have *facial* coordination involving the bridging phenolate O, and imidazolidine and imine nitrogen atoms. The bridging Co–O(phenolate) distances [av. 2.050 Å] are longer than terminal distances (av. 1.979 Å). The Co–N-(imidazolidine) [2.254(11) to 2.261(10) Å] and Co–N(imine) [2.019(10) to 2.026(12) Å] distances are clearly different. The terminal Co–O(carbonyl) distances [2.103(9) and 2.144(9)] are intermediate between the above two distances and the angle between the chelate rings of dfp^- is 160.94°. The template ligand in an "ice-cream cone" shape holds the Co(μ-OPh)Co unit in a space-filling model of the complex (Figure 4). Intramolecular hydrogen bonding was found between lattice water molecules and terminal phenolate oxygen atoms of ligand L^{3-} (Figure S2). A crystal-packing diagram along the *c* axis is shown in Figure S3.

Magnetochemistry of $[Co^{II}_2(\mu\text{-dfp})L]\cdot 3H_2O$ ($\mathbf{2}\cdot 3H_2O$)

The magnetic property of complex $\mathbf{2}\cdot 3H_2O$ was investigated by means of bulk magnetization methods. Measurements were collected under a constant magnetic field of 0.5 T in the 4.5–300 K temperature range. The effective magnetic moment at 300 K of **2** is measured to be $6.24\mu_B$ against $5.38\mu_B$ at 4.5 K per molecule of the complex. The temperature dependence of the magnetic moment was analyzed by the expression $\chi_M = f(T)$[32] derived from the Van Vleck equation, where

$$\chi_M = \frac{2Ng^2\beta^2}{kT}\left[\frac{14 + 5\exp(-6J/kT) + \exp(-10J/kT)}{7 + 5\exp(-6J/kT) + 3\exp(-10J/kT) + \exp(-12J/kT)}\right]$$

The results for the complex are represented in Figure 5 in the form of χ_M and μ_{eff} versus T plots (χ_M is the molar paramagnetic susceptibility and μ_{eff} is the effective magnetic moment). The parameters emerging from this fit are J = –0.38 cm^{-1} and g = 2.27, and $N\alpha$ was set to 0 cm^3 mol^{-1}. The experimental behavior clearly shows that the intramolecular coupling is antiferromagnetic, leading to a ground state S = 3/2:3/2 dimer model applicable because the distortion from octahedral symmetry is so large.[2a] So the small antiferromagnetic intramolecular coupling might be ascribed to the Co^{II}–O–Co^{II} angles formed by the phenolate bridges (between 95.79° and 97°), which are within the range predicted to lead to antiferromagnetic interactions in Co^{II}_2 systems.[33]

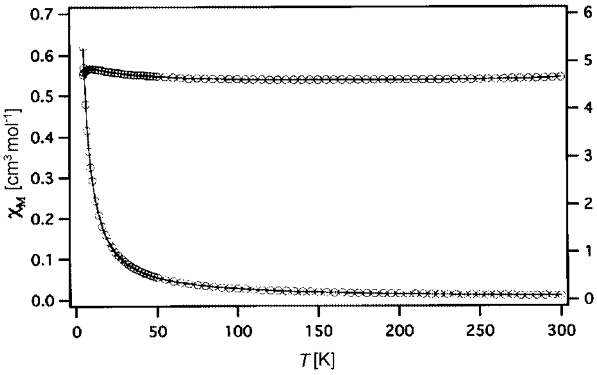


Figure 5. Plot of the temperature dependence of χ_M and μ_{eff} for complex $\mathbf{2}\cdot 3H_2O$.

Conclusions

We have shown that both solvent-derived and externally added templates control the synthesis of a new family of $Co^{III}Co^{III}$ and $Co^{II}Co^{II}$ complexes using a binucleating imidazolidinyl ligand H_3L. As part of the interesting chemistry of the ligand L^{3-} with Co^{II} and Co^{III}, we have shown that in situ generation of methoxide in the presence of N_3^- and external addition of diformylphenolate and bis(benzylimino)phenolate to the system inhibit the imidazolidine ring hydrolysis of the L^{3-} and lead to the high-yield formation of the assemblies $[Co^{III}_2(\mu\text{-OMe})L(N_3)_2]$ (**1**), $[Co^{II}_2(\mu\text{-dfp})L]\cdot 3H_2O$ ($\mathbf{2}\cdot 3H_2O$), and $[Co^{II}_2(\mu\text{-bip})L]\cdot 3H_2O$ ($\mathbf{3}\cdot 3H_2O$). The crystal structure of **1** shows that aerial oxidation in the presence of anions yields the Co_2 complex in 3+ oxidation state, whereas this oxidation is prevented when bisdidentate bridging template ligands are used. Interconversion of the templates within this family of the complexes is not permissible, which in turn identifies the templates as an integral part of these assemblies. Magnetic measurements indicate that complex **2** exhibits weak antiferromagnetic coupling between the Co^{II} centers bridged by two phenolate groups of different origin. We are currently working to exploit the asymmetry induced by external bridges in this reaction system in order to induce the formation of heterometallic and high nuclearity complexes.

Experimental Section

Materials and Physical Measurements: The chemicals used were obtained from the following sources: Triethylenetetramine, sodium azide, and cobalt acetate tetrahydrate from S.D. Fine Chem. (India) and 2-hydroxybenzaldehyde from SRL (India). 2,6-Diformyl-4-methylphenol (Hdfp) and 2,6-bis(benzyliminomethyl)-4-methylphenolate (Hbip) were prepared by the literature procedures.[21,23] All other chemicals and solvents were reagent-grade materials and were used as received without further purification. The elemental analyses (C,H,N) were performed with a Perkin–Elmer model 240C elemental analyzer. FTIR spectra were recorded with a Perkin–Elmer RX1 spectrometer. The solution electrical conductivity and electronic spectra were obtained using a Unitech type U131C digital conductivity meter with a solute concentration of about 10^{-3} M and a Shimadzu UV 3100 UV/Vis/NIR spectrophotometer respectively. The room-temperature magnetic susceptibilities in the solid state were measured using a home-built Gouy balance fitted with a Polytronic d.c. power supply. The experimental magnetic susceptibilities were corrected for the diamagnetic response using Pascal's constants. Magnetic measurements were carried out on polycrystalline samples (about 30 mg) using a Quantum Design MPMS-5S SQUID magnetometer operating at a constant magnetic field of 5000 G between 4.5 and 300 K. The experimental magnetic moment was corrected for the diamagnetic contribution from the sample holder and the diamagnetic response from the sample, which was evaluated from Pascal's constants.

General: All experimental procedures were carried out under air at room temperature. The ligand H_3L {2-(2′-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine} was prepared according to a literature procedure.[8]

Synthesis of Complexes: One single high-yield method was followed for the synthesis and isolation of complexes **1**–**3**. For complex **1**, a nontemplate procedure was followed in which the methoxide template was generated in solution, while for **2** and **3** prior addition of template ligands was necessary. In the absence of these templates and in the presence of azides, only **1** is isolated exclusively. Details are given below for the representative cases.

[Co^{III}_2(μ-OMe)L(N_3)$_2$] (1): NaN_3 (0.13 g, 2.00 mmol) in MeOH was added dropwise to the methanolic solution (20 mL) of $Co(OAc)_2\cdot 4H_2O$ (0.5 g, 2.00 mmol) and stirred for 15 min. Methanolic solution (15 mL) of ligand H_3L (0.458 g, 1.00 mmol) was then added dropwise to the above solution, and stirring was continued in air for 1 h leading to the oxidation of both the metal ions to Co^{III}. After evaporation of the reaction mixture a brown solid was obtained (about 75% yield). The reaction in the presence of up to 6 mmol of NaN_3 yields complex **1** exclusively, with no sign of azido bridging. The solid was isolated, washed with cold methanol, and dried under vacuum over P_4O_{10}. $C_{28}H_{30}Co_2N_{10}O_4$ (688.48): calcd. C 48.84, H 4.39, N 20.34; found C 48.76, H 4.28, N 20.08. Selected FTIR bands (KBr): $\tilde{\nu}$ = 2025 (vs), 1629 (vs), 1531 (m), 1451 (s), 1322 (m), 1264 (m), 1146 (m), 1093 (m), 949 (m), 755 (m) cm^{-1}. Molar conductance, Λ_M (CH_3CN solution): 6 $ohm^{-1}cm^2mol^{-1}$. UV/Vis spectra (CH_3CN solution): λ_{max} (ε, $L mol^{-1}cm^{-1}$) = 639 (470), 349 (4600), 275 (7600) nm.

Caution! Metal azide complexes are potential explosives. Only a small amount of material should be prepared and handled with caution.

[Co^{II}_2(μ-dfp)L]·3H_2O (2·3H_2O): 2,6-Diformyl-4-methylphenol (Hdfp) (0.164 g, 1.00 mmol) in MeOH was added dropwise to a methanolic solution (50 mL) of $Co(OAc)_2\cdot 4H_2O$ (0.5 g, 2.00 mmol) for 15 min whilst stirring. Ligand H_3L (0.458 g, 1.00 mmol) in hot methanol (20 mL) was added to the resulting solution and the mixture was stirred for another 1 h. The resulting solution was filtered and left undisturbed to slowly evaporate. After 4 d, a red crystalline product was obtained (about 80% yield). The solid was isolated, washed with cold methanol, and dried under vacuum over P_4O_{10}. $C_{36}H_{39}Co_2N_4O_9$ (789.59): calcd. C 54.76, H 4.97, N 7.09; found C 54.66, H 4.88, N 6.92. Selected FTIR bands (KBr): $\tilde{\nu}$ = 3396 (b), 1625 (s), 1597 (s), 1528 (s), 1443 (s), 1397 (m), 1341 (m), 1230 (m), 1185 (m), 1146 (m), 1034 (m), 988 (m), 756 (m) cm^{-1}. Molar conductance, Λ_M (CH_3CN solution): 6 $ohm^{-1}cm^2mol^{-1}$. UV/Vis spectra (CH_3CN solution): λ_{max} (ε, $L mol^{-1}cm^{-1}$) = 562 (310), 375 (2400), 271 (12500) nm.

[Co^{II}_2(L)(μ-bip)]·3H_2O (3·3H_2O): 2,6-Bis(benzyliminomethyl)-4-methylphenolate (Hbip) (0.342 g, 1.00 mmol) was added dropwise to a methanolic solution (50 mL) of $Co(OAc)_2\cdot 4H_2O$ (0.5 g, 2.00 mmol) for 15 min whilst stirring. Ligand H_3L (0.458 g, 1.00 mmol) in hot methanol (20 mL) was added to the resulting solution and the mixture was stirred for another 1 h. The resulting solution was filtered and left undisturbed to slowly evaporate. After 7 d, a red crystalline product was obtained (about 75% yield). The solid was isolated, washed with cold methanol, and dried under vacuum over P_4O_{10}. $C_{50}H_{54}Co_2N_6O_7$ (968.88): calcd. C 61.98, H 5.61, N 8.67; found C 61.88, H 5.54, N 8.48. Selected FTIR bands (KBr): $\tilde{\nu}$ = 3422 (b), 1624 (vs), 1601 (s), 1560 (s), 1451 (vs), 1400 (m), 1320 (m), 1233 (m), 1028 (m), 754 (m) cm^{-1}. Molar conductance, Λ_M (CH_3CN solution): 8 $ohm^{-1}cm^2mol^{-1}$. UV/Vis spectra (CH_3CN solution): λ_{max} (ε, $L mol^{-1}cm^{-1}$) = 591 (361), 401 (2100), 274 (8700) nm.

CCDC-644647 (for **1**) and -644648 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Figures S1, S2, and S3.

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