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Enantiopure Mono- and Mixed-Valence Multinuclear Cobalt Complexes from Amino Alcohol Based Ligands

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Chiral amino alcohol based tridentate Schiff bases, derived from 5-OMe-, 5-H-, and 5-NO_2-substituted salicylaldehydes and (*S*)-(+)-2-phenylglycinol and (*S*)-(–)-2-amino-3-phenyl-1-propanol, were found to act as versatile ligands in their coordination behavior towards cobalt and gave a range of complexes like mononuclear low-spin Co^{III} complexes, mixed-valence trinuclear Co^{III}–Co^{II}–Co^{III} complexes, and a mixed-valence tetranuclear $(Co^{III})_3Co^{II}$ complex on 1:1 molar ratio reaction with $Co(CH_3COO)_2·4H_2O$ in methanol at room temperature. The steric and electronic properties of these ligands are found to control the overall geometry and nuclearity of the resulting complexes. 5-OMe-Substituted ligands ($\mathbf{H_2L^1}$ and $\mathbf{H_2L^2}$) gave mononuclear low-spin Co^{III} complexes $[CoL^1(HL^1)]·0.25DMF$ (**1**) and $[CoL^2(HL^2)]·0.25DMF$ (**2**). Single-crystal X-ray structure analysis of complex **2** revealed that the relevant complex crystallizes with four mononuclear units in the asymmetric unit ($Z' = 4$), and these units self-assemble through O–H···O hydrogen-bonding interactions resulting in the formation of homochiral supramolecular helices in the crystal lattice. The 5-H- and 5-NO_2-substituted ligands ($\mathbf{H_2L^3}$, $\mathbf{H_2L^4}$, $\mathbf{H_2L^5}$) afforded mixed-valence trinuclear Co^{III}–Co^{II}–Co^{III} complexes $[Co(CoL^3{}_2)_2·H_2O]·2DMF·2H_2O$ (**3**), $[Co(CoL^4{}_2)_2·H_2O]·2DMF·H_2O$ (**4**), and $[Co(CoL^5{}_2)_2·DMF]·2DMF·H_2O$ (**5**), respectively. Crystal structure analyses of complexes **3** and **5** revealed rare trinuclear geometries of these complexes, in which two terminal octahedral low-spin Co^{III} complexes act as chelating ligands for a central high-spin Co^{II} center through alkoxide bridging. For steric reasons, the central cobalt adopts a highly distorted geometry in these complexes viz. distorted trigonal bipyramidal in complex **3** and distorted square planar in complex **5**. The ligand $\mathbf{H_2L^6}$ gave an interesting tetranuclear mixed-valence complex, $H[Co(CoL^6{}_2)_3]·H_2O$ (**6**), in which three octahedral low-spin Co^{III} complexes act as ligands for a central high-spin Co^{II} center in distorted trigonal prismatic geometry. Interestingly, the three types (mononuclear: **1**, **2**; trinuclear: **3**, **4**, **5**; tetranuclear: **6**) of complexes showed large variations in their nuclearity and overall geometry despite the fact that the experimental conditions for all these complexes were identical. This fact highlights the influence of different substitutions on ligands in determining the final geometry of the resulting complexes in these reactions. Complexes **1**–**6** were characterized by elemental and routine spectral analyses. Compounds **2**, **3**, **5**, and **6** have been unequivocally characterized by single-crystal X-ray structure determinations as well. Chiral properties of these complexes were confirmed by circular dichroism (CD) spectral studies.

Introduction

Synthesis of enantiopure metal complexes having predetermined properties is an important task in modern chemistry; one successful approach towards this goal being the use of well designed chiral ligands.[1] The quest for the development of improved chiral ligand systems necessitates the identification of novel and versatile chiral sources, in addition to the traditional chiral pools such as natural amino acids.[2] Presently, chiral amino alcohols have emerged as a promising chiral source for the preparation of asymmetric catalysts, chiral auxiliaries, and biologically relevant compounds.[3] Schiff bases of chiral amino alcohols are widely employed in catalysis and complexes of these ligands with various metal ions have been successfully employed as catalysts for a number of asymmetric transformations.[4] A thorough understanding of the coordination properties of such ligands will, therefore, be of great importance in designing more efficient systems. Structural studies including single-crystal X-ray crystallography can reveal the collective as well as complex roles of various structure-directing elements (such as steric and electronic effects) of the ligand systems in determining the overall geometry, and hence properties, of the resulting complexes. However, the number of structurally characterized amino alcohol based chiral complexes is surprisingly limited in the literature.[5]

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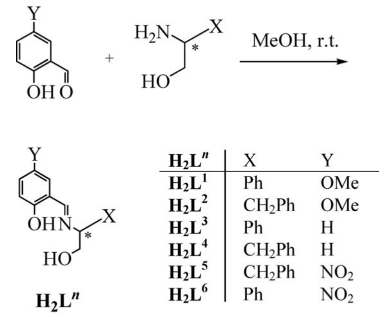
At the same time, identification of new cobalt-containing proteins in recent years (e.g., nitrile hydratase, methionine aminopeptidase etc.) points to the need to acquire a much wider knowledge of the coordination properties of cobalt in various ligand environments, especially chiral environments.[6] Chiral amino alcohol based Schiff bases, with their phenolic and alcoholic donor groups and potential for steric and electronic fine-tuning, are suitable candidates for bioinorganic modeling studies as well. In our efforts to understand the structure-directing effects of chiral amino alcohol based ligands on the coordination properties of biologically and catalytically relevant metal ions,[7] we report here the syntheses, crystal structures, and properties of some fascinating enantiopure cobalt complexes **1**–**6**, derived from chiral amino alcohol based Schiff bases **H_2L^1**–**H_2L^6** (Scheme 1).



H_2L^n	X	Y
H_2L^1	Ph	OMe
H_2L^2	CH_2Ph	OMe
H_2L^3	Ph	H
H_2L^4	CH_2Ph	H
H_2L^5	CH_2Ph	NO_2
H_2L^6	Ph	NO_2

$[CoL^1(HL^1)]\cdot 0.25DMF$	1
$[CoL^2(HL^2)]\cdot 0.25DMF$	2
$[Co(CoL^3{}_2)_2\cdot H_2O]\cdot 2DMF\cdot 2H_2O$	3
$[Co(CoL^4{}_2)_2\cdot H_2O]\cdot 2DMF\cdot H_2O$	4
$[Co(CoL^5{}_2)_2\cdot DMF]\cdot 2DMF\cdot H_2O$	5
$H[Co(CoL^6{}_2)_3]\cdot H_2O$	6

Scheme 1.

We have described herein how the steric and electronic properties of substituents ‘X’ and ‘Y’ on the ligand backbone (see Scheme 1) affect the overall geometry and nuclearity of this series of compounds **1**–**6** in identical experimental conditions. It was found that, the 5-OMe-substituted ligands (**H_2L^1** and **H_2L^2**) furnished mononuclear low-spin Co^{III} complexes $[CoL^1(HL^1)]\cdot 0.25DMF$ (**1**) and $[CoL^2(HL^2)]\cdot 0.25DMF$ (**2**). The 5-H- and 5-NO_2-substituted ligands (**H_2L^3**, **H_2L^4**, **H_2L^5**) are responsible for the isolation of mixed-valence trinuclear Co^{III}–Co^{II}–Co^{III} complexes $[Co(CoL^3{}_2)_2\cdot H_2O]\cdot 2DMF\cdot 2H_2O$ (**3**), $[Co(CoL^4{}_2)_2\cdot H_2O]\cdot 2DMF\cdot H_2O$ (**4**), and $[Co(CoL^5{}_2)_2\cdot DMF]\cdot 2DMF\cdot H_2O$ (**5**) respectively. Interestingly, the combination of X = Ph and Y = NO_2 (**H_2L^6**) afforded a tetranuclear mixed-valence compound $H[Co(CoL^6{}_2)_3]\cdot H_2O$ (**6**) in which three mononuclear low-spin Co^{III} complexes act as ligands for a central high-spin Co^{II} center that is in distorted trigonal prismatic geometry. The following sections describe and analyze the above-mentioned observations in detail.

Results and Discussion

Synthesis and Characterization of Chiral Ligands H_2L^1–H_2L^6

The chiral ligands (Scheme 1) were synthesized in good yields by the Schiff base condensation of 1 equiv. of salicylaldehyde/substituted salicylaldehyde with 1 equiv. of the respective chiral amino alcohol in methanol solutions at room temperature. The IR spectra of all the ligands show broad peaks in the range of 3210–3500 cm^{-1} because of the phenolic and alcoholic OH groups. Peaks observed around 1600, 1490, and 1450 cm^{-1} are most probably due to aromatic C=C stretching vibrations. These Schiff bases exhibit a ν(C=N) band in the range of 1626–1649 cm^{-1} and the peaks in the range 1028–1070 cm^{-1} are assigned to alcoholic C–O stretching. ν_{asym} and ν_{sym} stretches of the –NO_2 group present in ligands **H_2L^5** and **H_2L^6** appear at 1545, 1350 and 1543, 1346 cm^{-1} respectively.[8]

The electronic absorption spectra of the chiral Schiff base ligands **H_2L^1**–**H_2L^6** in acetonitrile solvent exhibit characteristic absorption bands at about 320 and 255 nm, which are assigned to transitions of the intramolecularly hydrogen-bonded salicylidenimino chromophore. These ligands also show circular dichroism (CD) spectra that have multiple Cotton effects corresponding to the electronic absorption maxima (see Figure S2 in the electronic supporting information for a representative CD and an electronic spectral curve for the ligand **H_2L^1**). The negative sign of these observed Cotton effect bands can be correlated with the absolute configuration of the respective amino alcohol moiety.[9]

Synthesis of Complexes 1–6

Complexes **1**–**6** were synthesized by reacting one molar equivalent of the corresponding Schiff base ligand with one molar equivalent of cobalt acetate tetrahydrate in methanol solutions at room temperature. The red-brown solutions thus obtained were evaporated completely and subsequently extracted with dichloromethane (DCM). The DCM solutions on evaporation gave dark red-brown solids that were recrystallized from dimethylformamide (DMF) solutions. Coordination of the imine nitrogen to the metal center is seen in the ν(C=N) IR band of the complexes in the range 1651–1641 cm^{-1}. In some complexes, this value is found to be slightly higher than that of the uncoordinated Schiff base. Although this is uncommon, it has been reported in the literature.[10] The strong band at ca. 1540 cm^{-1} is characteristic of the phenolic C–O stretching mode acquiring partial double bond character through conjugation with the imine system in chelate rings. The C=C stretch appears at ca. 1600 cm^{-1} as a shoulder band. Elemental analytical data of the complexes did not conform to a general molecular formula. Based on elemental and other characterization data, described in the following sections, it was found that complexes **1**–**6** showed variations in their nuclearity and overall geometry despite the fact that the experimental conditions were identical. It was also found that all the complexes contain at least one Co^{III} center in their molecular structure, probably formed by the oxidation of Co^{II} acetate used in the syntheses. Atmospheric oxygen is the possible oxidizing agent here, and this oxidation is facilitated by the alkoxide and phenoxide groups present on the ligands. **H_2L^1** and **H_2L^2** gave mononuclear low-spin Co^{III} complexes, while ligands **H_2L^3**, **H_2L^4**, and **H_2L^5** gave mixed-valence trinuclear Co^{III}–Co^{II}–Co^{III} complexes. The ligand **H_2L^6** gave an interesting tetranuclear cobalt complex with rather uncommon trigonal prismatic geometry around the central cobalt. Tetradentate Schiff base–oxovanadium complexes having electron-donating or -withdrawing groups at the 5-position of the salicylaldehyde moieties are reported to show similar structural diversity, where the 5-MeO-substituted complex is monomeric and the 5-H- and 5-NO$_2$-substituted complexes are found to be polymeric.[11]

In order to rule out the possibility that the observed changes in nuclearity of complexes **1**–**6** might have been caused by slight changes in the experimental conditions rather than the influence of ligand substitutions, the synthetic reactions of complexes **1**–**6** were carefully reproduced many times and in each case the reported products were obtained in good yields as the main product, confirming that the substitution on the ligand backbone is mainly responsible for the observed changes in nuclearity.

Electronic and Circular Dichroism Spectra of Complexes 1–6

The electronic and circular dichroism spectra of complexes **1**–**6** were recorded in acetonitrile solutions. The electronic spectra show two weak bands in the 650–700 nm and 520–535 nm ranges. These bands are tentatively assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ ligand field transitions respectively, characteristic of an octahedral Co^{III} center.[12] It appears that the relatively high intensities of these d-d

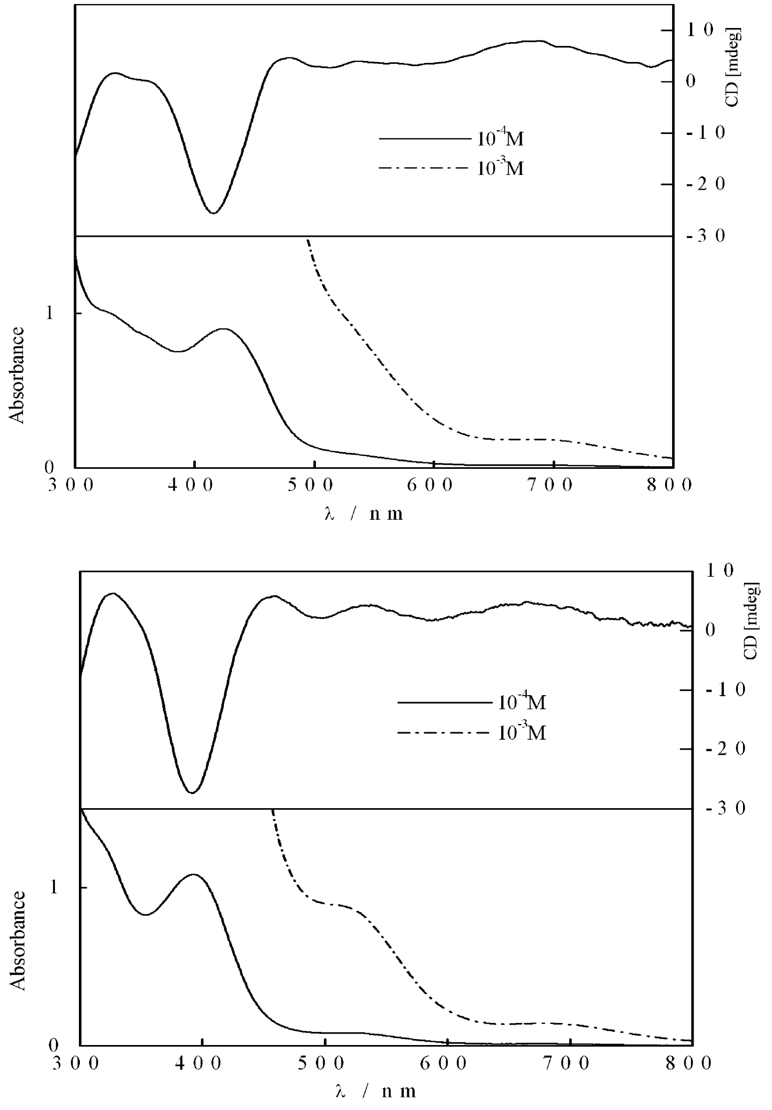


Figure 1. The electronic and circular dichroism spectra of complexes **1** (top) and **3** (bottom).

bands are due to strong tail-from-charge transfer transitions. The intense band observed around 400 nm is assigned to phenolate $(O^{-})p_{\pi} \rightarrow Co^{III}$ charge-transfer transition (LMCT). The other intense transitions in the spectra are assigned to intraligand charge-transfer transitions (ILCT). The transitions due to Co^{II} centers are not observed in mixed-valence complexes **3**–**6**, probably because these transitions might have been obscured by the intense absorptions due to Co^{III} centers of these complexes.[13] Two representative electronic absorption spectra are shown in Figure 1.

A general blueshift in band positions is observed for these complexes with electron-withdrawing substituents on ligands. This blueshift originating from the electron-withdrawing nature of the substituents has been observed previously in some similar complexes.[14]

The circular dichroism spectra of these complexes show bands corresponding to their respective electronic absorptions. The visible bands due to the d-d transitions are positive, while the charge transfer transitions appear as negative Cotton effects. The electronic and CD spectra of complexes **1**–**6** are similar despite their structural changes. The appearance of Co^{III} d-d bands for all six complexes confirms the presence of at least one Co^{III} center in each of the complexes. The representative CD curves are presented in Figure 1.

Magnetic Properties

The magnetic susceptibility measurements of complexes **1**–**6** were performed on powdered samples at room temperature. Complexes **1** and **2** were found to be diamagnetic, as expected for a low-spin Co^{III} state. Magnetic moments in the range of 3.4–5.1 BM were observed for complexes **3**–**6**, which indicate the presence of a high-spin Co^{II} center ($S = 3/2$) with three unpaired electrons in these complexes. The magnetic properties of polynuclear complexes are extremely sensitive to structural modifications. The Co^{II} center present in these complexes (**3**–**6**) is found to exist in a variety of structural environments ranging from distorted trigonal bipyramidal in **3** to distorted trigonal prismatic in complex **6**. Therefore, the large spread of the observed μ_{eff} values for these complexes is attributed to their geometric distortions that influence the magnitude of the ligand field splitting. The observed low effective magnetic moment for complex **3** (3.4 B.M.) implies that the orbital contribution to the spin-only value (3.87 B.M.) is fairly small in this complex.

Crystal Structure of Complex 2

Single crystals of complex **2** suitable for X-ray crystallography were grown from DMF solutions by slow evaporation method. The complex crystallizes in the chiral space group orthorhombic $P2_12_12_1$. The asymmetric unit consists of four mononuclear cobalt complexes and one solvent DMF molecule. The cobalt complexes are almost octahedral in shape and their tridentate ONO donor Schiff base ligand binds the metal in a meridional manner. The molecular geometry and the atom-labeling scheme for a representative mononuclear unit are given in Figure 2 (see Table S4 in the electronic supporting information for selected bond lengths and bond angles for this complex). Although the respective hydrogen atoms are not located in the difference Fourier maps, it is assumed that in each mononuclear unit one of the ligands is doubly deprotonated while the second

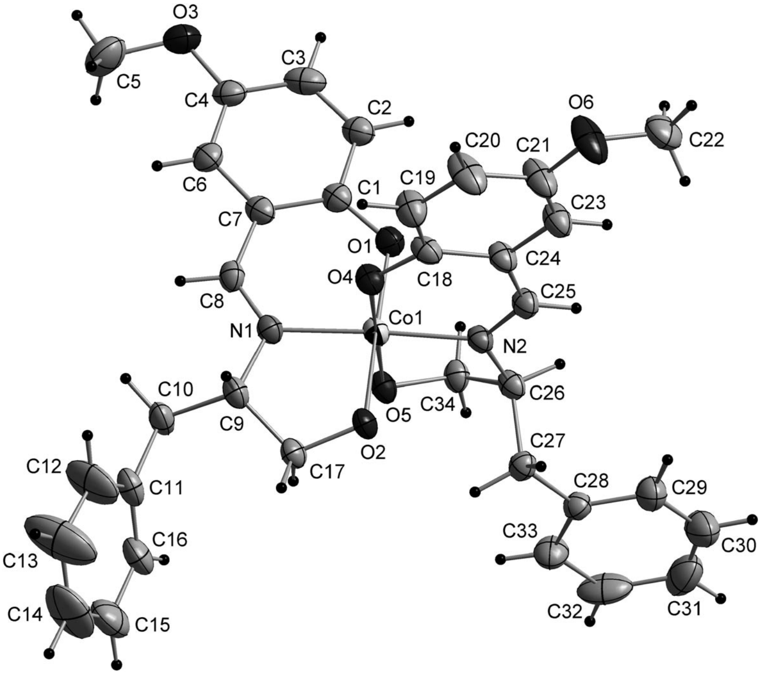
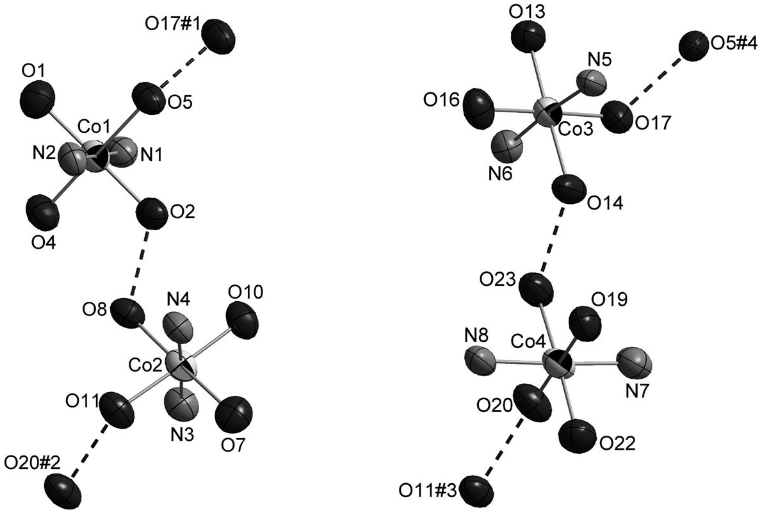


Figure 2. Molecular structure of a representative mononuclear unit of complex **2** showing atom-labeling scheme. Thermal ellipsoids are represented by their 30% probability level.



(a) (b)

Figure 3. O–H···O hydrogen-bonding interaction pattern in the asymmetric unit of complex **2** resulting in hydrogen-bonded dimers.

one is singly deprotonated. It is observed that in each mononuclear unit one of the Co–O_{alk} bond lengths is considerably longer than the other [for example Co1–O2 1.906(5) Å while Co1–O5 1.944(4) Å], probably for the above-mentioned reason. This conclusion is also consistent with the overall charge balance of the system. The average Co–O_{phe} [1.882(5) Å], Co–O_{alk} [1.932(5) Å], and Co–N_{imi} [1.902(6) Å] bond lengths are within the range reported for low-spin Co^{III} complexes.[15] The room-temperature magnetic-moment measurements showed that the complex is diamagnetic, also indicating a low-spin Co^{III} complex.

The four mononuclear cobalt complexes present in the asymmetric unit self-assemble through intermolecular O–H···O interactions resulting in the formation of homochiral supramolecular helices in the crystal lattice (Figures 3 and 4).

Each mononuclear complex contains two alcoholic oxygen atoms, one of which is protonated and the other deprotonated. The protonated alcoholic oxygen atom acts as the hydrogen-bond donor while the deprotonated alcoholic oxygen atom acts as the acceptor. The four mononuclear complexes can be labeled as Co1, Co2, Co3, and Co4 (Figure S4, supporting information). The complexes Co1 and Co2 are interconnected by a strong hydrogen bond between alcoholic oxygen atoms O2 and O8 [O2···O8 2.442(6) Å] and exist as a hydrogen-bonded dimer as shown in Figure 3 (a). Similarly, the mononuclear units Co3 and Co4 also exist as a dimer (Figure 3, b), formed by the hydrogen-bonding interactions between alcoholic oxygen atoms O14 and O23 [O14···O23 2.386(7) Å]. These independent dimers are further linked to each other through two O–H···O interactions [O5···O17 2.464(6) Å and O11···O20 2.425(6) Å] resulting in supramolecular hydrogen-bonded homochiral helices in the relevant crystal lattice, as presented in Figure 4. The resulting O–H···O interactions are strong, as evident from the rather short O···O distances.

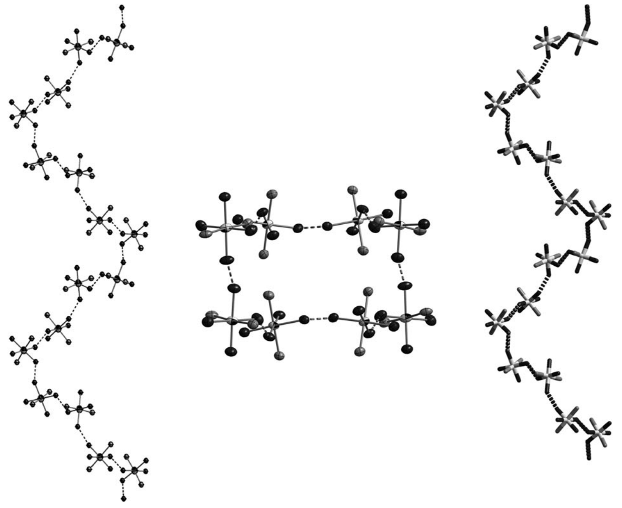


Figure 4. View illustrating intermolecular O–H···O hydrogen-bonding interactions among adjacent molecules that lead to the formation of supramolecular homochiral helices in the crystal lattice of complex **2**. Left: ball-and-stick representation. Right: wire frame representation of the helix. Middle: view down the crystallographic *b* axis showing the helical groove.

One full turn of the helix contains eight mononuclear complexes (Figure 4, left and right), that is, each hydrogen-bonded dimer (Figure 3) in the asymmetric unit repeats twice in one helical turn. The pitch distance is found to be 25.508 Å. The path of the helix can be traced by following the hydrogen bonds counter-clockwise around the twofold screw axis of the helix. The complex is chiral and the crystal contains only one enantiomer of the complex. This local chirality translates into the formation of only left-handed helices on the supramolecular level. Figure 4 clearly depicts the hydrogen-bonding pattern in the asymmetric unit and the mode of propagation of helices in the crystal lattice.

Crystal Structure of Complex 3

The single crystals of complex **3** suitable for X-ray analysis were grown from DMF solutions by a slow evaporation method. The complex crystallizes in noncentrosymmetric triclinic space group $P\bar{1}$. X-ray analysis shows that the asymmetric unit of complex **3** contains one trinuclear cobalt complex, two solvent DMF molecules, and two water molecules. The molecular structure, with atom-labeling scheme of the complex, is shown in Figure 5. The relevant crystallographic parameters are given in Table 1 (see Table S5 in the supporting information for selected bond lengths and angles observed in complex **3**).

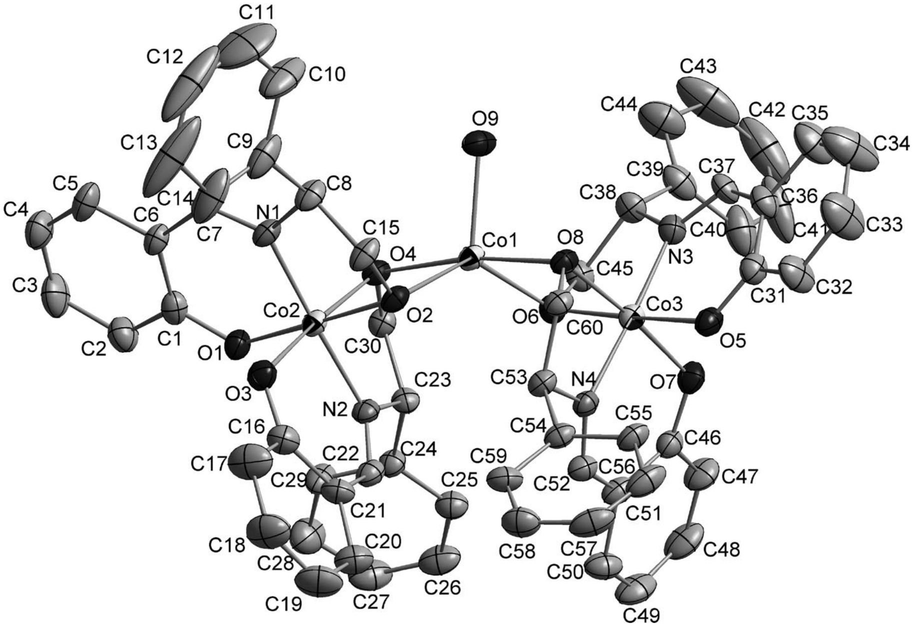


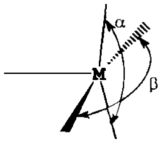
Figure 5. Molecular structure of complex **3** showing atom-labeling scheme. Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are represented by their 30 % probability level.

Table 1. Summary of X-ray collection data.

Complex	2	3	5	6
Empirical formula	$C_{139}H_{147}Co_4N_9O_{25}$	$C_{66}H_{72}Co_3N_6O_{13}$	$C_{73}H_{79}Co_3N_{11}O_{20}$	$C_{90}H_{75}Co_4N_{12}O_{25}$
Formula mass	2579.38	1334.09	1607.26	1960.34
Crystal system	orthorhombic	triclinic	monoclinic	tetragonal
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1$	$P4_12_12$
λ [Å]	0.71073	0.71073	0.71073	0.71073
a [Å]	21.5421(11)	11.4737(7)	12.352(11)	18.5054(5)
b [Å]	25.5084(13)	12.4004(8)	24.736(19)	18.5054(5)
c [Å]	25.6047(13)	13.2286(8)	13.085(5)	46.257(3)
α [°]		105.0090(10)		
β [°]		92.7810(10)	90.22(6)	
γ [°]		93.7460(10)		
V [Å^3]	14069.9(12)	1809.87(19)	3998(5)	15840.7(11)
Z	4	1	2	4
μ [mm^{-1}]	0.532	0.739	0.690	0.459
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.218	1.224	1.335	0.822
T [°C]	25	25	25	25
Scan type	ω	ω	ω	ω
Independent reflections	147193 (R_{int} = 0.098)	18905 (R_{int} = 0.023)	9308 (R_{int} = 0.158)	183227 (R_{int} = 0.124)
Observed reflections	27690	13920	9304	19330
Number of parameters	1598	735	909	591
Goodness-of-fit	0.99	1.03	1.02	0.92
R_1, wR_2 [$I > 2\sigma(I)$]	0.078, 0.183	0.072, 0.179	0.083, 0.176	0.082, 0.209
Largest diff. peak and hole [e Å^{-3}]	1.05 and –0.33	0.80 and –0.32	0.57 and –0.61	0.97 and –0.42
Absolute structure parameter	–0.001(16)	0.036(17)	–0.02(3)	–0.02(2)

In the trinuclear geometry of complex **3**, the two terminal cobalt centers are distorted octahedral with N_2O_4 coordination sphere. The doubly deprotonated Schiff base ligands act as tridentate donors and bind the cobalt ions in a meridional fashion. The square base of the octahedron is made up of two phenoxo oxygen atoms and two alkoxide oxygen atoms, about which the two imine nitrogen atoms are situated at *trans* positions. The average $Co–N_{imi}$ [1.909(5) Å for Co2 and 1.904(6) Å for Co3], $Co–O_{phe}$ [1.880(5) Å for Co2 and 1.900(5) Å for Co3], and $Co–O_{alk}$ [1.914(5) Å for Co2 and 1.904(4) Å for Co3] distances observed are consistent with the corresponding values observed in related octahedral Co^{III} complexes.[15] The observed distortions from ideal octahedral geometry are caused by the small bite angle of the Schiff base group [N2–Co2–O4 83.6(2)° for Co2 and N4–Co3–O8 83.9(2)° for Co3].

These two terminal octahedral cobalt complexes act as chelating ligands to the central cobalt Co1 through alkoxide oxygen bridging. The central cobalt is five-coordinated with an $\{O_5\}$ coordination sphere. The five coordination sites are satisfied by four bridging alkoxide oxygen atoms and a water molecule. The geometry around Co1 can be considered as distorted trigonal bipyramidal in which the axial Co–O bond lengths Co1–O4 and Co1–O8 [av. 2.113(5) Å] are significantly longer than the other three Co–O bonds, which are considered as equatorial bonds [av. 1.994(5) Å]. The distortion along the axial direction is also obvious from the O4–Co1–O8 angle of 170.38(17)°. The τ value for the central cobalt, as explained by Addison et al.,[16] is calculated to be 0.66, as shown in Scheme 2, confirming a distorted trigonal bipyramidal (tbp) geometry around it (τ = 1 for ideal trigonal bipyramidal geometry, τ = 0 for ideal square-pyramidal geometry). This distortion from ideal tbp geometry can be rationalized by the formation of two constrained four-membered rings around Co1 (Figure 5) as a result of the alkoxide oxygen bridging. Steric factors caused by the bulky terminal cobalt centers may also contribute to the observed distortions. The two four-membered rings attached to the central cobalt are inclined to each other at an angle of 54°.



$$\tau = \frac{\alpha-\beta}{60}$$

Scheme 2.

The Co–O bond lengths [av. 2.042(5) Å] around the central cobalt Co1 are significantly longer than those around the terminal cobalt ions, indicating that the central cobalt is divalent while the terminal ones are trivalent. The variations in $Co^{III}–O$ and $Co^{II}–O$ bond lengths can be expected because the Shannon radius of Co^{II} (0.885 Å) is larger than that of Co^{III} (0.75 Å).[17] The trimer is therefore formulated as a $Co^{III}–Co^{II}–Co^{III}$ mixed-valence complex, as shown in Figure 5. This assignment is also supported by the fact that there should be two Co^{3+} ions and one Co^{2+} ion in complex **3** to balance the net charge of 8^- created by four doubly deprotonated ligands in the molecule.

The average Co···Co separation is found to be 3.011(11) Å in complex **3**, which is considerably smaller than the Co···Co separations [3.821[18a], 3.872,[18b] and 3.066[18c] Å] found in similar mixed-valence trinuclear cobalt complexes. The Co2–Co1–Co3 angle is found to be 136.33(3)°.

There are hydrogen-bonding interactions among the coordinated water molecule and the solvent DMF molecules in the molecular structure of complex **3**. The two DMF molecules are connected to the coordinated water molecule through O–H···O hydrogen-bonding interactions. The relevant O···O distances are O9···O10#1 2.591(9) Å and O9···O11#2 2.610(10) Å where #1 = *x*, 1 + *y*, –1 + *z* and #2 = *x*, 1 + *y*, *z* (see Figure S5, electronic supporting information, for hydrogen-bonding in compound **3**).

Crystal Structure of Complex 5

X-ray analysis on a single crystal of compound **5** indicates that the asymmetric unit of complex **5** contains one trinuclear cobalt complex, two solvent DMF molecules, and one solvent water molecule. The complex crystallizes in the monoclinic space group $P2_1$. Crystallographic details are presented in Table 1.

Quite similar to the structure of complex **3**, the molecular structure of complex **5** also consists of a trinuclear cobalt geometry, as shown in Figure 6. The two terminal cobalt complexes in this molecule are in distorted octahedral N_2O_4 coordination sphere and have doubly deprotonated amino alcohol Schiff base ligand $\mathbf{H_2L^5}$ satisfying the coordination sites around the cobalt in a meridional manner. The deviations of bond angles from ideal octahedral values are within ±7° (see supporting information, Table S6). The average $Co–N_{imi}$ [1.887(10) Å for Co2 and 1.912(9) Å for Co3], $Co–O_{phe}$ [1.884(8) Å for Co2 and 1.895(8) Å for Co3], and $Co–O_{alk}$ [1.898(8) Å for Co2 and 1.901(7) Å for Co3] distances observed for the terminal cobalt centers are consistent with corresponding values observed in related octahedral Co^{III} systems.[15]

The two terminal octahedral Co complexes act as chelating units for the central cobalt Co1 through alkoxide oxygen bridging. As expected, the central cobalt is five-coordinated, the fifth coordination site being occupied by a solvent DMF molecule. Two four-membered rings are formed around Co1 as a result of the chelation through alkoxide oxygen atoms by the two terminal cobalt octahedral complexes. Because of this, Co1 assumes a highly distorted geometry, which is almost intermediate between trigonal bipyramidal (tbp) and square-pyramidal (sp), as evidenced by the τ value of 0.40 (see Scheme 2).[16] It can be concluded from this value that the distortion is more towards square-pyramidal in this case. The two four-membered rings attached to the central cobalt are inclined to each other at an angle of 44°.

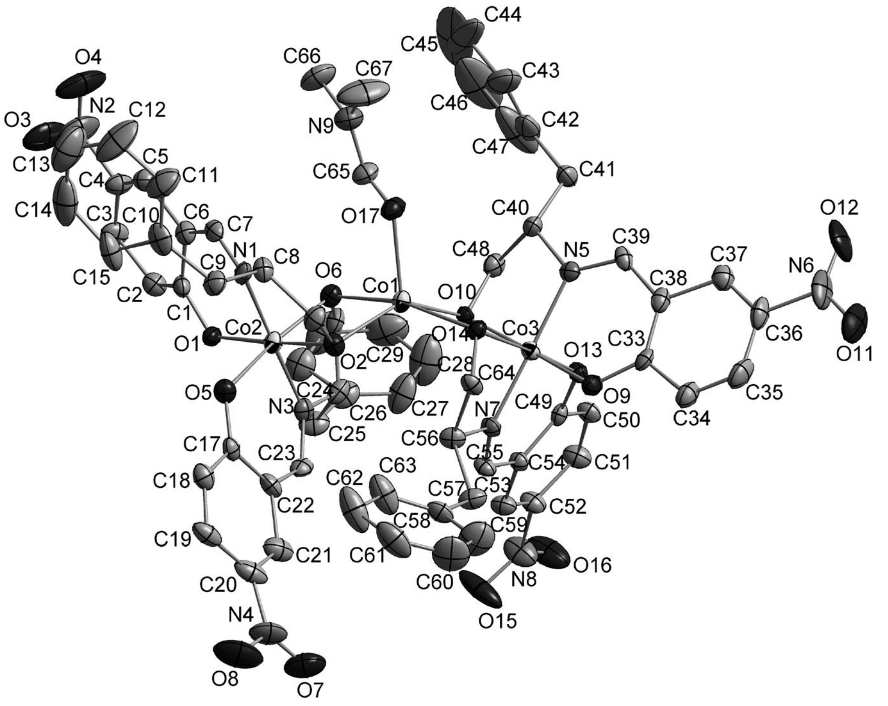


Figure 6. Molecular structure of complex **5** showing atom-labeling scheme. Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are represented by their 30% probability level.

As in the case of complex **3**, the bond lengths around the central cobalt Co1 are significantly longer than those around the terminal cobalt centers in complex **5** as well, indicating that the central cobalt is divalent while the terminal ones are trivalent. The average Co–O distance for Co1 is 2.039(9) Å. Based on the bond length analysis, charge balance, and magnetic moment measurement studies, the trimer in complex **5** can be regarded as a Co^{III}–Co^{II}–Co^{III} mixed-valence complex.

Similar to complex **3**, the Co···Co separations of 2.992(3) Å [Co2···Co1] and 2.969(3) Å [Co3···Co1] are found to be smaller than the Co···Co separations reported for similar mixed-valence systems.[18] The Co2–Co1–Co3 angle is 140.01(8)°.

Crystal Structure of Complex 6

The single crystals of complex **6** suitable for X-ray analysis were grown by slow evaporation of DMF solutions. The complex crystallizes in the chiral tetragonal space group $P4_12_12$. The molecular structure and atom-labeling scheme of the complex are presented in Figure 7.

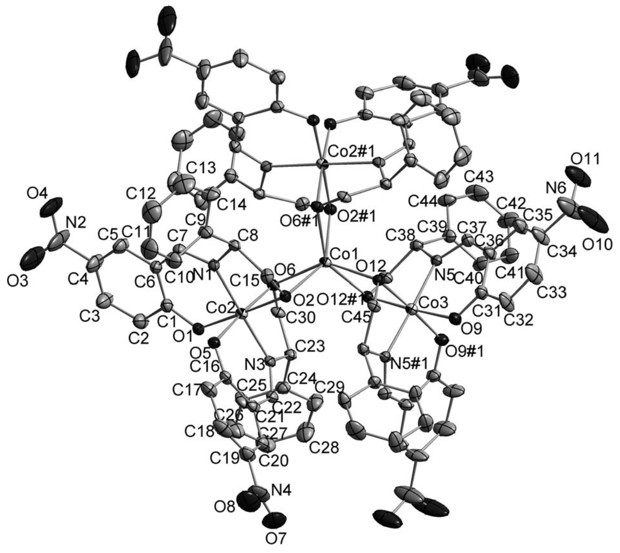


Figure 7. Molecular structure of complex **6** showing atom-labeling scheme. Symmetry-generated atoms are mostly unlabeled. Hydrogen atoms and solvent water molecule are omitted for clarity. Thermal ellipsoids are represented by their 20% probability level.

The asymmetric unit contains half of the complex molecule and a solvent water molecule. The crystal structure reveals an interesting tetranuclear geometry for complex **6**, in which three mononuclear cobalt complexes act as chelating ligands for a central cobalt ion. The terminal cobalt complexes are almost octahedral in shape, having two ONO donor Schiff base ligands satisfying the coordination sites of each cobalt in a meridional style.

The central cobalt Co1 is six-coordinated. The coordination polyhedron exhibits, surprisingly, a distorted trigonal prismatic (tp) geometry, which is rather scarce for polynuclear cobalt complexes. Four chelating alkoxide oxygen atoms [O2, O6, O12, and O12#1] from cobalt centers Co2 and Co3 form the square base for the trigonal prism. The oxygen atoms O2#1 and O6#1 from the third cobalt center Co2#1, occupy the remaining two vertices to complete the trigonal prismatic coordination sphere around the central Co1 as shown in Figure 8.

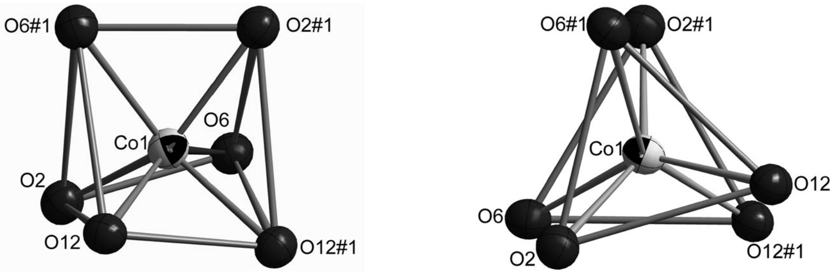


Figure 8. Left: coordination sphere depicting the distorted trigonal prismatic geometry around the central cobalt in complex **6**. Right: view down the trigonal faces of the coordination sphere showing distortion from ideal trigonal prismatic geometry.

The two trigonal faces of the trigonal prism (made up of oxygen atoms O2, O6#1, O12 and O2#1, O12#1, O6) are not equilateral and the square base also shows distortion from ideal geometry. The torsion angle involving opposing corners and the centroids of the trigonal faces are 17.39°, 17.39°, and 16.50° (see Figure 8, right). The distortion from the ideal trigonal prismatic geometry is possibly due to the severe steric overcrowding caused by the three bulky cobalt complexes that act as ligands for the central cobalt ion.

The average Co–N_{imi} [1.897(5) Å for Co2, Co2#1 and 1.875(4) Å for Co3], Co–O_{phe} [1.899(4) Å for Co2, Co2#1 and 1.899(4) Å for Co3], and Co–O_{alk} [1.885(4) Å for Co2, Co2#1 and 1.883(4) Å for Co3] distances observed for terminal cobalt complexes are comparable to the corresponding values observed in related octahedral Co^{III} systems[15] (see supporting information for selected bond lengths and bond angles (Table S7) for complex **6**). The average Co–O bond length of 2.148(3) Å around Co1 is found to be considerably longer than those around the terminal cobalt atoms. By the same argument given in the case of complexes **3** and **5**, it can be assumed that the central cobalt is in 2+ oxidation state. The steric crowding might have caused an additional increase in length of these bonds compared to those in complexes **3** and **5**.

Oxidation state assignment in complex **6** is also supported by the magnetic moment measurements and electronic spectroscopic studies. The electronic spectrum of the complex is similar to the mononuclear Co^{III} complexes **1** and **2**, which indicates the presence of Co^{III} units in the complex. Also the complex shows a net magnetic moment of 5.1 B.M. at room temperature, corresponding to the presence of a high-spin Co^{II} center. If all the tridentate ligands are doubly deprotonated in the molecule, there will be an excess of one negative charge in the complex. It is assumed that this extra negative charge might have been compensated for by one proton (probably because of single deprotonation of one of the ligands) at an unknown position in the complex. A similar situation is reported in the literature for a mononuclear Co^{III} complex with a similar ligand system.[19]

Calculations using the CALC VOID option in PLATON[20] showed a potential solvent access area of 8601.5 Å^3 (54.3%) per unit cell of the complex. This fact is also supported by the relatively low ρ_{calcd} value of 0.822 g cm^{-3} observed by the X-ray analysis. This void is created as a result of intermolecular C–H···O hydrogen-bonding interactions of the complex with its surrounding molecules, generating a three-dimensional hydrogen-bonded network in the crystal lattice (Figure 9). In these interactions, the oxygen atoms O3, O7, and O10 of the –NO_2 group act as the hydrogen-bond acceptor while the aromatic carbon atoms C28, C3, and C11 act as the donors. The relevant hydrogen-bonding

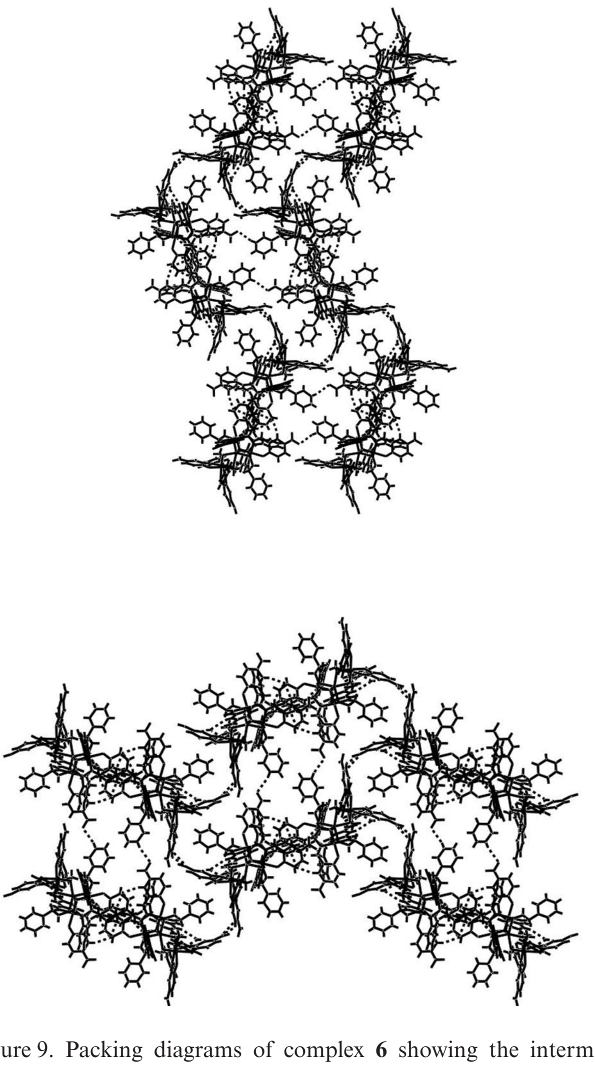


Figure 9. Packing diagrams of complex **6** showing the intermolecular C–H···O hydrogen-bonding interactions that lead to the formation of voids in the crystal lattice. View along the *a* axis (top) and view along the *b* axis (bottom).

parameters are given in the supporting information (Table S8). The extension of hydrogen-bonding interactions in a three-dimensional manner thus leads to porosity in the crystal lattice with an overall solvent access area of above 50% in the unit cell. This area is partly occupied by solvent water molecules. The solvent water oxygen O13 is involved in C–H···O hydrogen-bonding interactions with the complex molecule carbons C20 and C22.

Conclusions

Many interesting observations are made in this study using simple chiral Schiff base ligands and cobalt acetate. The basic coordination sites and geometries of the ligands **H_2L^1** to **H_2L^6** are kept the same, changing the substitution on the salicylaldehyde part and the length of the amino alcohol side chain. It is found that these changes control the overall coordination geometries of the resulting cobalt complexes even though the experimental conditions were identical. Complexes of ligands with unsubstituted and 5-nitro-substituted salicylaldehydes prefer multinuclear arrangement while the methoxy-substituted derivatives prefer mononuclear arrangement. In complexes **1**–**6**, the ligands contain both phenolic and alcoholic OH groups. Although both phenol and alkoxy groups can act as bridging functionalities, in these complexes the phenolic oxygen atoms do not act as a bridging group. In complexes **3**–**6** only alkoxide oxygen atoms were found to act as a bridging group. We can assume that the bridging ability of alkoxide oxygen atoms predominates in these complexes probably because of factors like steric and overall crystal packing effects.

In the multinuclear complexes studied here, the high-spin cobalt(II) adopts geometries ranging from distorted trigonal bipyramidal (tbp) and distorted square-pyramidal (sp) to distorted trigonal prismatic (tp). One of the reasons for such distortions may be steric effects caused by the bulky octahedral cobalt(III) complexes acting as ligands. These new edge-sharing octahedral-tbp/sp/tp-octahedral complexes **3**–**6** are complementary to the previous reports of edge-sharing octahedral-tetrahedral-octahedral and face-sharing all-octahedral trinuclear complexes.[21] From the present study, it is also clear that alkoxide oxygen atoms are capable of stabilizing high-spin cobalt(II) ions in a variety of rare geometrical arrangements.

High-spin Co^{II} has a definite preference for octahedral over trigonal prismatic geometry. The previously reported trigonal prismatic complexes of Co^{II} are mostly made up of rigid multidentate ligands.[22] The structure of complex **6** demonstrates that even bulky coordination complexes can stabilize such a geometry around high-spin Co^{II}, despite its preference for octahedral geometry. The extensive hydrogen-bonding interactions and the crystal-packing forces might have played some role in dictating such a geometry around the central cobalt in complex **6**.

The nitro-substituted ligands **H_2L^5** and **H_2L^6** gave both tri- and tetranuclear complexes. Here the steric effect of the lengthy side arm might have played a crucial role in dictating the said geometries. The lengthy CH_2Ph group creates more steric crowding around the central cobalt in complex **5**, unlike the Ph-substituted derivative in complex **6**, thus preventing another octahedral complex from approaching and coordinating to it.

The crystal structures of complexes **3** and **5** belong to the limited number of structurally characterized trinuclear cobalt complexes with mixed oxidation states. There are two main reported classes of trinuclear cobalt complexes of mixed-spin states. One includes mixed-valence trinuclear complexes of the form $Co^{III}(S = 0)$–$Co^{II}(S = 3/2)$–Co^{III} ($S = 0$),[13,18f] and another, mixed-spin trinuclear complexes of the form Co^{II} ($S = 1/2$)–Co^{II} ($S = 3/2$)–Co^{II} ($S = 1/2$).[23] The trinuclear complexes **3**–**5** discussed here belong to the former category.

Finally, it has been shown that the tridentate chiral Schiff base ligands **H_2L^1**–**H_2L^6** are very versatile in their coordination behavior towards cobalt and can readily form stable mono-, tri-, and tetranuclear chiral complexes with interesting structural features. Besides the isolation, characterization, and analysis of properties of chiral mono-, tri-, and tetranuclear cobalt complexes, we have demonstrated that the introduction of a different substitution on the ligand backbone can result in unexpected structural modifications of resulting complexes.

Experimental Section

General Information: Microanalytical (C,H,N) data were obtained with a FLASH EA 1112 Series CHNS Analyzer. A Shimadzu 3101-PC UV/Vis/NIR spectrophotometer was used to record the electronic spectra. Infrared spectra were recorded by using KBr pellets with a Jasco-5300 FTIR spectrophotometer. ^1H NMR spectra in $CDCl_3$ solutions were recorded with a Bruker DRX-400 spectrometer, using $Si(CH_3)_4$ as an internal standard. Room temperature solid-state magnetic susceptibilities were measured by using a Sherwood Scientific magnetic susceptibility balance. The CD spectra were measured in solution phase with a JASCO J-810 spectropolarimeter. Salicylaldehyde, 5-nitrosalicylaldehyde, 5-methoxysalicylaldehyde, (*S*)-(+)-2-phenylglycinol, and (*S*)-(–)-2-amino-3-phenyl-1-propanol were purchased from Lancaster (India) and used as received. Solvents used for UV/Vis and CD analyses were of HPLC grade and procured from E. Merck (India). All other chemicals were of analytical grade and were used without further purification.

Synthesis of Chiral Schiff Bases H_2L^1–H_2L^6: The synthesis and characterization of chiral Schiff bases **H_2L^3**, **H_2L^4**, **H_2L^5**, and **H_2L^6** have been reported elsewhere.[7]

H_2L^1: (*S*)-(+)-2-Phenylglycinol (0.137 g, 1 mmol) and 5-methoxysalicylaldehyde [2-hydroxy-5-methoxybenzaldehyde] (0.152 g, 1 mmol) were stirred together in methanol (15 mL) for 3 h at room temperature. The resulting yellow solution was filtered and the filtrate was kept open at room temperature for slow evaporation. A yellow solid, thus obtained, was washed with hexane and dried at room temperature. Yield 0.25 g, 92%. $C_{16}H_{17}NO_3$ (271.31): calcd. C 70.83, H 6.32, N 5.16; found C 70.77, H 6.25, N 5.11. IR (KBr): $\tilde{\nu}$ = 3485, 2860, 1635, 1589, 1491, 1272, 1157, 1068, 1028, 902, 831, 790, 761, 700, 534, 457 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3 H, OCH_3), 3.92–3.94 (d, *J* = 6.5 Hz, 2 H, CH_2), 4.46–4.49 (t, *J* = 6.44 Hz, 1 H, CH), 6.78–6.94 (m, 3 H, Ar), 7.26–7.39

(m, 5 H, Ar), 8.45 (s, 1 H, HC=N) ppm. UV/Vis (CH_3CN): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 343 (5039), 258 (10309) nm. CD (CH_3CN, 10^{-4} M): λ_{max} (mdeg) = 343 (–12.70), 258 (–19.80) nm.

H_2L^2: (*S*)-(–)-2-Amino-3-phenyl-1-propanol (0.151 g, 1 mmol) and 5-methoxysalicylaldehyde (0.152 g, 1 mmol) were stirred together in methanol (15 mL) for 3 h at room temperature. The resulting yellow solution was filtered and the filtrate was kept open for slow evaporation. A yellow semi-solid was obtained and washed with hexane and dried at room temperature. Yield: 0.26 g, 90%. $C_{17}H_{19}NO_3$ (285.34): calcd. C 71.56, H 6.71, N 4.91; found C 71.3, H 6.56, N 5.01. IR (KBr): $\tilde{\nu}$ = 3422, 1635, 1591, 1493, 1379, 1334, 1271, 1224, 1159, 1037, 908, 821, 761, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.8–3.0 (m, 2 H, CH_2), 3.51 (m, 1 H, CH), 3.73 (s, 3 H, OCH_3), 3.77–3.82 (m, 2 H, CH_2-OH), 6.57–6.95 (m, 3 H, Ar), 7.13–7.27 (m, 5 H, Ar), 8.03 (s, 1 H, HC=N) ppm. UV/Vis (CH_3CN): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 343 (5025), 258 (7916), 230 (20892) nm. CD (CH_3CN, 10^{-4} M): λ_{max} (mdeg) = 343 (–11.6), 258 (–19.2) nm.

H_2L^5: (*S*)-(–)-2-Amino-3-phenyl-1-propanol (0.151 g, 1 mmol) and 5-nitrosalicylaldehyde (0.167 g, 1 mmol) were stirred together in methanol (15 mL) for 3 h at room temperature. The resulting yellow solution was filtered and the filtrate was kept for 2 d in an open beaker for slow evaporation. The yellow precipitate of **H_2L^5** thus obtained was washed with hexane and dried at room temperature. Yield 0.27 g, 90%. $C_{16}H_{16}N_2O_4$ (300.31): calcd. C 63.99, H 5.37, N 9.33; found C 64.05, H 5.29, N 9.18. IR (KBr): $\tilde{\nu}$ = 3470, 1649, 1618, 1543, 1487, 1446, 1404, 1346, 1226, 1134, 1064, 941, 904, 835, 756, 729, 700, 630 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.97 (m, 2 H, CH_2-Ph), 3.65 (m, ^{1}H, CH), 3.86 (m, 2 H, CH_2-OH), 6.92 (d, 1 H, Ar, *ortho* to OH), 7.2 (m, 5 H, Ar), 8.04 (s, 1 H, HC=N), 8.06 (d, 1 H, Ar, *ortho* to NO_2), 8.15 (m, 1 H, Ar, *ortho* to NO_2) ppm. UV/Vis (CH_3CN): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 401 (6950), 325 (9931), 260 (17447), 240 (17111) nm. CD (CH_3CN, 10^{-4} M): λ_{max} (mdeg) = 401 (–2.66), 320 (–4.66), 260 (–5.85), 240 (–3.85) nm.

Synthesis of Cobalt Complexes 1–6: All six cobalt complexes **1**–**6**, reported here, were prepared according to the following general procedure.

$(CH_3COO)_2Co\cdot 4H_2O$ (0.249 g, 1 mmol) was added to a methanolic solution (25 mL) of the respective chiral ligand (1 mmol). The mixture was stirred at room temperature in air overnight. The resultant dark red-brown solution was evaporated to dryness using a rotavapor and a vacuum pump. The solid thus obtained was extracted with dichloromethane and evaporated to give a red-brown microcrystalline solid, which was recrystallized from a solution of DMF.

[CoL^1(HL^1)]·0.25DMF (1): Yield 0.23 g, 74%. $C_{32}H_{31}CoN_2O_6\cdot 0.25C_3H_7NO$ (616.81): calcd. C 63.77, H 5.35, N 5.11; found C 64.06, H 5.29, N 5.23. IR (KBr): $\tilde{\nu}$ = 2928, 1635, 1539, 1469, 1423, 1298, 1259, 1219, 1157, 1033, 947, 819, 769, 702, 528, 418 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$): 255 (35880), 315 (7686), 418 (3803), 535 (423), 700 (88) nm. CD (CH_3CN, 10^{-4} M): λ_{max} (mdeg): 275 (–21.6), 417 (–26.13), 535 (4.14), 692 (8.05) nm.

[CoL^2(HL^2)]·0.25DMF (2): Yield 0.22 g, 69%. $C_{34}H_{35}CoN_2O_6\cdot 0.25C_3H_7NO$ (644.86): calcd. C 64.72, H, 5.74, N, 4.89; found C 64.48, H 5.39, N 4.44. IR (KBr): $\tilde{\nu}$ = 3414, 3028, 2924, 1635, 1537, 1464, 1385, 1304, 1255, 1217, 1157, 1084, 1035, 814, 744, 700, 532, 466 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 255 (35471), 315 (7544), 420 (3914), 535 (435), 700 (96) nm. CD (CH_3CN, 10^{-4} M): λ_{max} (mdeg) = 292 (–9.15), 415 (–10.14), 520 (0.62), 685 (6.40) nm.

[Co(CoL$^3{}_2$)$_2$·H$_2$O]·2DMF·2H$_2$O (3): Yield 0.26 g, 77%. $C_{66}H_{72}Co_3N_6O_{13}$ (1334.11): calcd. C 59.42, H 5.44, N 6.30; found C 59.05, H 5.15, N 6.11. IR (KBr): $\tilde{\nu}$ = 3416, 3051, 2918, 2854, 1633, 1597, 1533, 1493, 1454, 1439, 1385, 1344, 1317, 1253, 1195, 1147, 1124, 1095, 1028, 945, 896, 831, 752, 704, 650, 628, 592, 534 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 252 (87930), 317 (13220), 398 (9402), 525 (867), 690 (138) nm. CD (CH_3CN, 10^{-4} M): λ_{max} (mdeg) = 262 (–24.88), 282 (–18.84), 394 (–27.62), 535 (4.19), 668 (4.55) nm. Room temp. magnetic moment = 3.4 B.M.

[Co(CoL$^4{}_2$)$_2$·H$_2$O]·2DMF·H$_2$O (4): Yield 0.26 g, 76%. $C_{70}H_{78}Co_3N_6O_{12}$ (1372.20): calcd. C 61.27, H 5.73, N 6.12; found C 61.69, H 5.53, N 5.98. IR (KBr): $\tilde{\nu}$ = 3024, 2916, 1635, 1599, 1535, 1448, 1388, 1315, 1195, 1147, 1082, 956, 844, 748, 700, 580, 524, 468 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 251 (76170), 322 (10950), 394 (8070), 526 (1284), 705 (400) nm. CD (CH_3CN, 10^{-4} M): λ_{max} (mdeg) = 280 (–4.19), 394 (–13.27), 516 (0.22), 675 (3.48) nm. Room temp. magnetic moment = 4.35 B.M.

[Co(CoL$^5{}_2$)$_2$·DMF]·2DMF·H$_2$O (5): Yield 0.28 g, 70%. $C_{73}H_{79}Co_3N_{11}O_{20}$ (1607.27): calcd. C 54.55, H 4.95, N 9.59; C 54.78, H 4.83, N 9.13. IR (KBr): $\tilde{\nu}$ = 2922, 1647, 1601, 1545, 1473, 1386, 1313, 1097, 947, 831, 754, 702, 659, 489 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 240 (72860), 317 (21190), 385 (50960), 520 (1013), 650 (350) nm. CD (CH_3CN, 10^{-4} M): λ_{max} (mdeg) = 259 (–12.26), 390 (–13.17), 522 (1.96), 660 (4.83) nm. Room temp. magnetic moment = 4.25 B.M.

H[Co(CoL$^6{}_2$)$_3$]·H$_2$O (6): Yield 0.22 g, 68%. $C_{90}H_{75}Co_4N_{12}O_{25}$ (1960.36): calcd. C 55.14, H 3.86, N, 8.57; found C 55.01, H 3.92, N 8.23. IR (KBr): $\tilde{\nu}$ = 3566, 2924, 1647, 1602, 1548, 1473, 1383, 1313 (nitro), 1132, 1101, 1026, 951, 827, 756, 696, 655, 540 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 243 (120830), 315 (38660), 387 (92940), 520 (1560), 650 (478) nm. CD (CH_3CN, 10^{-4} M): λ_{max} (mdeg) = 262 (–45.73), 383 (–40.37), 530 (8.25), 660 (11.00) nm. Room temp. magnetic moment = 5.1 B.M.

X-ray Crystallography: A summary of the crystallographic data for compounds **2**, **3**, **5**, and **6** is given in Table 1. Data for complexes **2**, **3**, and **6** were collected at room temperature with a Bruker SMART APEX CCD area detector system [λ(Mo-K_α) = 0.71073 Å], graphite monochromator, 2400 frames were recorded with an ω-scan width of 0.3°, crystal-detector distance 60 mm, collimator 0.5 mm. The data were reduced using SAINTPLUS[24] and a multiscan absorption correction using SADABS[24] was performed. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares procedures using SHELX-97 programs.[25] Hydrogen atoms were introduced on calculated positions and included in the refinement riding on their respective parent atoms. The absolute configurations for the complex molecules were successfully determined by refining the respective Flack parameters.[26] In the case of complex **2**, all the non-hydrogen atoms are refined anisotropically. The hydrogen atoms associated with some of the alcoholic oxygen atoms were not located in the difference Fourier maps. For complex **3**, all the non-hydrogen atoms except that of the uncoordinated solvent molecules are refined anisotropically. Some of the benzene rings show disorder and some restraints were applied. Hydrogen atoms were not located in association with coordinated and solvent water molecules. For complex **6**, the R_{int} value was considerably higher (0.1235). Such a high R_{int} value is attributed to the long *c* axis [46.257(3) Å] and the subsequent difficulty in neatly resolving adjacent reflections and to the low diffraction power of the relevant crystal characterized by a large fraction of weak intensities. Also this particular complex contains a large amount of void space. All the non-hydrogen atoms except the water oxygen are refined anisotropically. The hydrogen atoms associated with the solvent water molecule are not located in the difference Fourier maps. Single crystals of complex **5** were grown by slow evaporation of a dimethylformamide solution. Unit cell determination and the data collection were performed on an Enraf–Nonius Mach3 single-crystal diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). An empirical absorption correction was applied to the data based on the ψ-scans of three reflections.[27] Programs of WinGX[28] were used for data reduction and absorption correction. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELX-97 program.[25] All the non-hydrogen atoms except the uncoordinated solvent molecules were refined anisotropically. Some benzene rings show disorder and some restraints were applied. Hydrogen atoms were not located in association with water molecule oxygen atom. A high R_{int} value (0.1510) observed in this case is probably due to the low diffraction power of the crystal characterized by a large fraction of weak intensities.

CCDC-651783 (for **2**), -651784 (for **3**), -651785 (for **5**), and -651786 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Detailed synthesis and characterization of the Schiff bases (ligands) $\mathbf{H_2L^1}$–$\mathbf{H_2L^6}$; representative ^{1}H NMR spectrum of $\mathbf{H_2L^6}$; representative UV and CD spectra of $\mathbf{H_2L^1}$; crystal structure description of the ligand $\mathbf{H_2L^5}$; additional figures for crystal structures of the complexes; tables (selected bond lengths and angles) for compounds **2**, **3**, **5**, and **6**; a table for hydrogen-bonding parameters for compound **6**; a table for summary of electronic spectra and room temperature magnetic moments for compounds **1**–**6**.

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