

Azido, Cyanato, and Thiocyanato Coordination Induced Distortions in Pentacoordinated $[\text{Co}^{\text{II}}\text{A}(\text{bip})]_2$ ($\text{A} = \text{NCS}^-$, N_3^- , or NCO^-) Complexes

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Keywords: N,O ligands / Bridging ligands / Cobalt / Structure elucidation / Magnetic properties

A new family of distorted pentacoordinate $[\text{Co}_2]$ complexes was prepared and structurally characterized. In $[\text{Co}^{\text{II}}\text{A}(\text{bip})]_2\cdot\text{S}$ (**1–3**) [$\text{A} = \text{NCS}^-$, N_3^- , NCO^- ; $\text{S} = \text{dmf}$, MeOH , dcm ; $\text{Hbip} = 2,6\text{-bis(phenylmethyliminomethyl)-4-methylphenol}$], the nonbonded $\text{Co}\cdots\text{Co}$ separations are in the 3.243 to 3.254 Å range, and the pseudohalide-coordinated Co^{II} ions are asymmetrically doubly bridged by the phenolate oxygen atoms of the ligand. The complementary *basal–apical* (*b–a*) and *apical–basal* (*a–b*) coordination modes of the phenolate

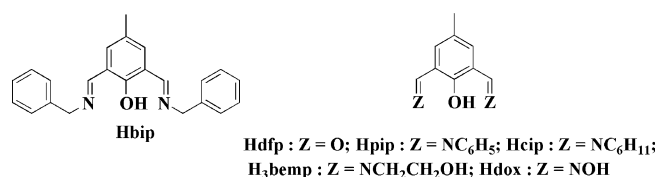
bridges of bip^- offer one O and two N donors for metal-ion coordination. In the three dinuclear complexes, the *h.s.* Co^{II} ions are coupled antiferromagnetically to yield a singlet ground state. The solid-state variable-temperature magnetic susceptibility measurement data on the complexes were fitted to an isotropic Heisenberg dimer model that allowed estimation of the antiferromagnetic interactions for **1–3**.

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Introduction

The synthesis and synthetic applications of high-spin Co^{II}_2 complexes have been the subject of current research in controlled preparation, molecular structure, and magnetism.^[1–5] These complexes have attracted attention because of their fascinating magnetic properties as well as their biological relevance. In the first context, dinuclear Co^{II} complexes may act as mimics of the active biosites such as in methionine aminopeptidase^[6] and can show DNA cleavage activity.^[7] Methionine aminopeptidase is known to be a Co_2 metallohydrolase responsible for removal of the *N*-terminal methionine from protein chains and contains cobalt ions in distorted octahedral and trigonal bipyramidal geometries.^[8] High-spin Co^{II}_2 complexes show difficulties in magnetic analysis because of orbital angular momentum,^[9] which is completely or partially quenched in a ligand field of a cer-

tain symmetry.^[10] Several reports have been made on octahedral (O_h) or tetrahedral (T_d) symmetries,^[11–16] and only few cases are known in distorted trigonal-bipyramidal (TBP) or square-pyramidal (SP) symmetries.^[17–22] The magnetic properties of Co^{II} in the low TBP or SP symmetries can be treated in a simple manner, as the ground term does not have first-order orbital angular momentum; thus, a spin-only treatment is valid.^[9,10,23] Recently, it was reported that low-spin square-planar Co^{II}_2 diporphyrin complexes having a Pac-Man-like cleft can show interesting dioxygen reduction chemistry.^[24] Because of these different features of the Co^{2+} ion, earlier we studied its coordination behavior and reactivity toward imidazolidinyl trisphenol ligands.^[25] Recently, we also reported the successful use of one 2,6-diformyl-4-methylphenol (Hdfp) or 2,6-bis(benzyliminomethyl)-4-methylphenol (Hbip) (Scheme 1) as coligands for the preassembly of Co^{II}_2 units as a template for binding of imidazolidinyl trisphenol ligand.



Scheme 1.

The main objectives of the present investigation are (i) to scrutinize the efficacy of the bridging phenolate-only ligands to assemble discrete $[\text{Co}_2\text{L}_2]$ -type complexes, (ii) to examine the role of different pseudohalides for geometric distortions in such an assembly process, and (iii) to stabilize

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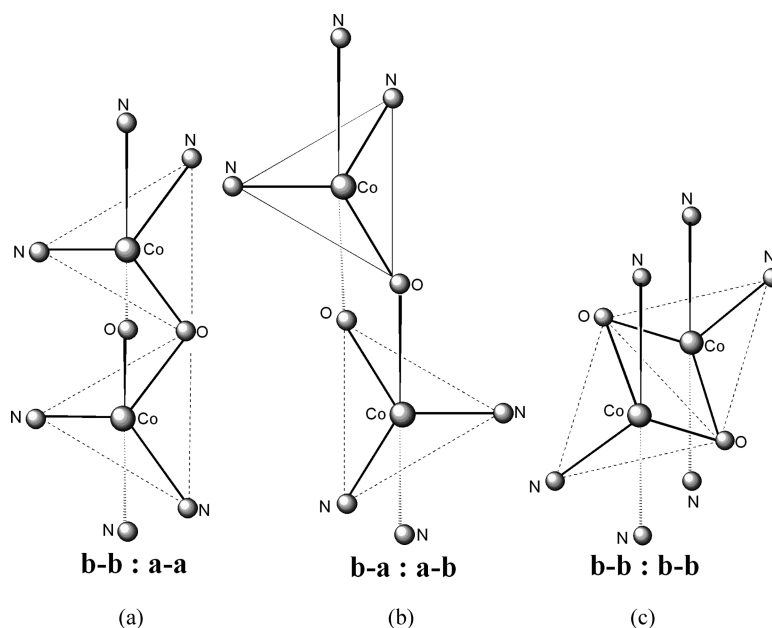
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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejic.200900577>.



Scheme 2. Possible binding mode of bridging phenolate groups of two ligands.

the 2+ oxidation states of cobalt in highly distorted coordination environments using nonplanar (*basal-apical*) phenolate bridges (Scheme 2). We have successfully achieved our goal by using Hbip.

The choice of the ligands are important, as they can exhibit nonplanar binding modes and nonregular coordination geometries, which are often noticed in dinuclear Co^{II} active sites in proteins. Thus, the manipulation of the binding ability of the donor atoms of the ligand system around the cobalt ions is crucial to control the metal-ion coordination geometries. Co^{II} ions can adopt various geometries such as tetrahedral, square-planar, square-pyramidal, and trigonal bipyramidal, in addition to their distorted versions, depending upon the steric and electronic nature of the donor atoms.^[26–32] Newer types of coordination behavior of Hbip (Scheme 1) have been explored for various reasons, including their importance in coordination chemistry, molecular magnetism, and catalysis.^[33] Herein three complexes $[\text{Co}^{\text{II}}\text{A}(\text{bip})_2\text{S}]$ (**1–3**) ($\text{A} = \text{NCS}^-$, N_3^- , or NCO^- ; $\text{S} = \text{dmf}$, MeOH , dcm) derived from the nonplanar assembly of two Hbip ligands following three different pseudohalide coordination driven routes are reported. Selective binding of a single pseudohalide anion to each Co^{II} ion is responsible for the nonplanar orientation of the ligands, resulting in distortions of the pentacoordinate coordination geometries unknown in synthesis but well recognized in biology. Complexes **1–3** were crystallographically characterized and their magnetic properties in highly distorted environments were scrutinized.

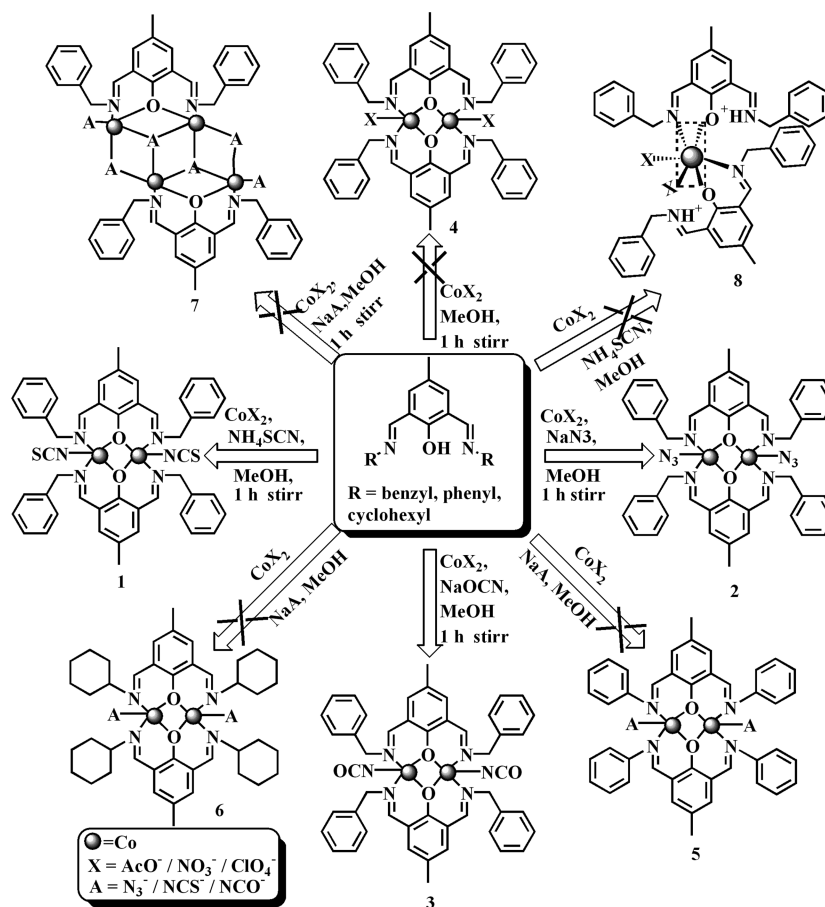
Results and Discussion

Syntheses and Spectroscopic Characterizations

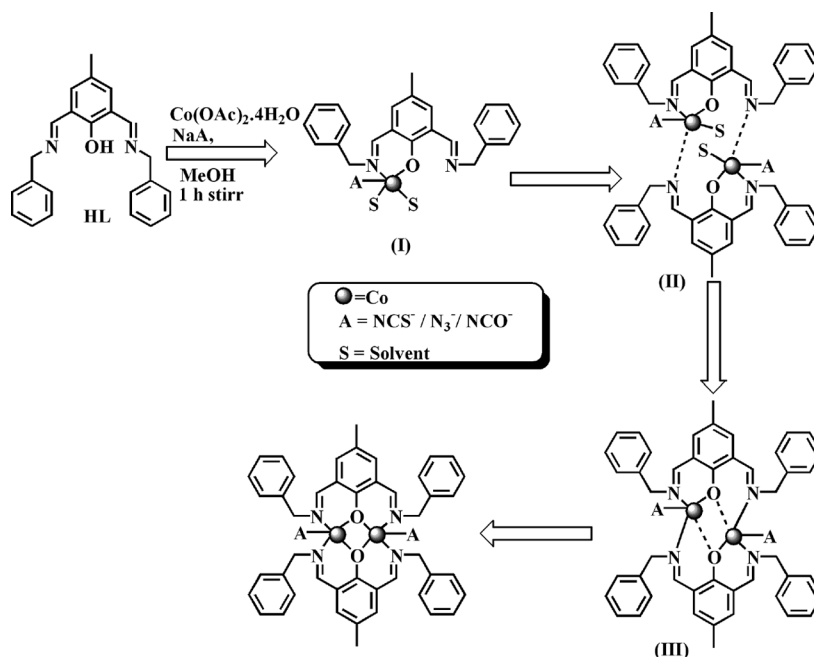
The synthesis and initial purification of Hbip [2,6-bis(phenylmethyliminomethyl)-4-methylphenol] (Scheme 1) is

analogous to that reported earlier in the literature^[34] and its reaction with cobalt(II) salts was investigated in the presence of three pseudohalides. Satisfactory routine characterizations were made from melting-point determinations, elemental analyses, FTIR, and ^1H and ^{13}C NMR spectroscopy. A general procedure, as depicted in Scheme 3, was followed for the synthesis of complexes **1–3** in the presence of stoichiometric amounts of NH_4SCN , NaN_3 , and NaOCN , cobalt(II) salts, and Hbip in CH_3OH at room temperature in air.

This synthetic procedure allows the synthesis of neutral $[\text{Co}^{\text{II}}\text{A}(\text{bip})_2]$ complexes with high purity and in very good yield. Addition of an excess amount of NH_4SCN , NaN_3 , or NaOCN could not yield any isothiocyanato-, azido-, or cyanato-bridged di- or tetracobalt complex. (Scheme 3) With a similar type of di-Schiff base H_3bemp ligand (Scheme 1) having two more terminal alcohol groups, we earlier showed the $\mu_3\text{-OMe}$ bridge driven aggregation of a $[\text{Co}^{\text{III}}_4]$ species.^[35] Exactly similar to this, we tried to obtain $\mu_3\text{-OMe/A}$ bridged compound **7** (Scheme 3). We were unable to characterize and crystallize any of such compounds. The macrocyclic template effect was observed earlier in the closely related dioxime-based ligand Hdox (Scheme 1) for an octahedral high-spin dicobalt(II) complex.^[36] Expected compound **4** was not isolated from the reaction of Hbip with $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, or $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the absence of A^- in MeOH . In different crystallizing solvents and solvent mixtures, X-ray quality single crystals of **1–3** were obtained. Weakly coordinating or noncoordinating anions like ClO_4^- , NO_3^- , or AcO^- bearing cobalt salts do not yield any characterizable product. Only the external addition of NaN_3 , NaOCN , or NH_4SCN to the reaction mixture led to the high-yield formation of pentacoordinate dicobalt assemblies of nonregular coordination geometries. This verifies the superior coordination ability of



Scheme 3. Schematic representation for preferred ligand and pseudohalide binding for $[\text{Co}_2]$ assembly in three cases compared to other unknown species.



Scheme 4. Likely mechanism of formation of $[\text{CoA}(\text{bip})]_2\text{S}$ (1–3) ($\text{A} = \text{NCS}^-$, N_3^- , or NCO^- ; $\text{S} = \text{dmf}$, MeOH , dcm) by dimerization of two initially formed monocobalt species through diphenolate *basal-apical* (*b-a*) bridges.

NCS[−], N₃[−], or NCO[−] as coligands against AcO[−], NO₃[−], or ClO₄[−].^[37] Presumably coordination of one A[−] and two solvent molecules to each cobalt center and dimerization of the neutral [Co^{II}A(bip)S₂] species lead to the formation of 1–3 through phenolate *basal-apical* connection of the strong–weak category (I to III in Scheme 4). The neutral complexes are either insoluble or sparingly soluble in water and common organic solvents, but they are soluble in polar organic solvents such as CH₂Cl₂, dmf, and dmsol.

The compounds appear to be stable both in the solid state and in solution, and they all melt above 350 °C. The molar conductivity (Λ_M) values of all three complexes are in the range 6–10 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ (28 °C) and correspond to electroneutral character.

Steric crowding around the imine nitrogen atoms plays an important role towards the solid-state crystallization of the complexes. Substitution of benzylamine in the synthesis of Hbip by aniline and cyclohexylamine give Hpip and Hcip, in which the imine nitrogen atoms are more crowded (Scheme 3). Reaction of these two ligands with cobalt(II) salts in presence of three different pseudohalides gave no solid isolable product. Thus, the presence of methylene spacers in the bip[−] ligands contribute to the distortion of the pentacoordinate geometries around the cobalt(II) ions (vide supra). In MeOH, the reaction of either Co(OAc)₂·4H₂O or Co(NO₃)₂·6H₂O or Co(ClO₄)₂·6H₂O and NH₄SCN or NaN₃ or NaOCN followed by the addition of a methanolic solution of Hbip in a 1:2:2 molar ratio does not yield mononuclear complex **8** bearing the zwitterionic ligand H₂bip⁺ (Scheme 3).

Infrared Spectroscopy

The sharp peaks in the FTIR spectra of 1·dmf, 2·CH₃OH, and 3·CH₂Cl₂ at 1628, 1627, and 1629 cm^{−1}, respectively, are characteristic of the C=N functionalities of the deprotonated ligand bip[−]. The $\nu(\text{C}=\text{N})$ stretching frequency of the free ligand is observed at 1636 cm^{−1}. Complex 1·dmf records one strong band at 2070 cm^{−1} for the $\nu(\text{CN})$ stretching of the terminally coordinated NCS[−]^[38] ion, but the $\nu(\text{CS})$ stretching frequency in the 700–825 cm^{−1} region could not be identified with certainty in the presence of strong absorptions by the organic ligand in this region.^[39] Terminal coordination of azide groups to cobalt(II) ions in 2·CH₃OH shows a very strong sharp band at 2050 cm^{−1} and a weak band at 1345 cm^{−1} for the $\nu_{\text{as}}(\text{N}_3^-)$ and $\nu_{\text{s}}(\text{N}_3^-)$ stretching vibrations, respectively.^[40] NCO[−]-bonded 3·CH₂Cl₂ registers a strong band at 2207 cm^{−1} for the asymmetric $\nu(\text{CN})$ stretching vibration and a medium intensity peak at 1345 cm^{−1}, which can be attributed to the pseudo-symmetric $\nu(\text{CO})$ stretching. The bending mode δ_{NCO} of the coordinated cyanate anion could not be located in the 600–825 cm^{−1} region under the absorptions of the bip[−] ion.^[41]

Electronic Spectroscopy

The electronic spectra of 1–3 in dmf solutions show similar spectral features in the 250–600 nm region. The intense

bands at ca. 250 and ca. 325 nm can be assigned to the $\pi \rightarrow \pi^*$ transition associated with the azomethine group.^[42,43] The moderately intense band at ca. 400 nm can be assigned to charge-transfer (CT) bands centered at the Co^{II} center and coordinated to bip[−]. A solution of **1** registers the d–d transition band at 578 nm ($\epsilon = 199 \text{ L mol}^{-1}\text{cm}^{-1}$) and CT bands at 398 ($\epsilon = 7360 \text{ L mol}^{-1}\text{cm}^{-1}$), 326 ($\epsilon = 8590 \text{ L mol}^{-1}\text{cm}^{-1}$), and 250 nm ($23870 \text{ L mol}^{-1}\text{cm}^{-1}$). The only d–d transition may be assigned to the $^4\text{A}'_2(\text{F}) \rightarrow ^4\text{A}'_2(\text{P})$ transition.^[44] A dmf solution of **2** exhibits all the above-mentioned electronic transitions at 578 ($\epsilon = 439 \text{ L mol}^{-1}\text{cm}^{-1}$), 398 ($\epsilon = 3683 \text{ L mol}^{-1}\text{cm}^{-1}$), 326 ($\epsilon = 4016 \text{ L mol}^{-1}\text{cm}^{-1}$), and 252 nm ($\epsilon = 14787 \text{ L mol}^{-1}\text{cm}^{-1}$). Compound **3** showed the corresponding transitions at 581 ($\epsilon = 291 \text{ L mol}^{-1}\text{cm}^{-1}$), 400 ($6721 \text{ L mol}^{-1}\text{cm}^{-1}$), 327 ($4231 \text{ L mol}^{-1}\text{cm}^{-1}$), and 251 nm ($21692 \text{ L mol}^{-1}\text{cm}^{-1}$), respectively.

Description of the Structures

Single crystals suitable for X-ray structure determinations were obtained by slow evaporation of a dmf solution of **1**, a dcm/MeOH (1:1) solution of **2**, and a dmf/dcm solution of **3** after a week. Selected interatomic distances and angles are collected in Table 1, and the crystallographic data are summarized in Table 2.

The atom labeling scheme and molecular views (ORTEP) of the complexes are shown in Figures 1–3. The three different solvents, dmf, MeOH, and dcm, either in pure form or in a mixture, play important roles in the crystallization process. Quality single crystals suitable for X-ray diffraction analysis are only obtained from the above-stated choices of single solvent and solvent mixtures.

[Co^{II}(NCS)(bip)]₂·dmf (1·dmf)

The molecular structure of [Co^{II}(NCS)(bip)]₂ is shown in Figure 1 together with the atom labeling scheme used. The structure consists of a [Co^{II}(NCS)(bip)]₂ dinuclear complex. Each cobalt atom is coordinated by the two imine nitrogen atoms of two ligands, two phenolate oxygen atoms of two ligands, and one nitrogen end of the NCS[−] group. The four-membered ring formed by the two cobalt atoms and two phenolate oxygen atoms of the bridge is essentially planar, and none of the atoms deviate from the least-squares plane by more than 0.936 Å. This [Co₂O₂] core is formed from asymmetric [Co1–O1 1.979(3), Co1–O2 2.142(3), Co2–O1 2.136(3), and Co2–O2 1.976(3) Å] *basal-apical* bridging by two phenolate oxygen atoms, and the two cobalt(II) centers are separated by 3.24 Å (Supporting Information, Figure S1), which is different from the situation found in other phenolate-oxygen-bridged dinuclear cobalt(II) complexes.^[45,46] This asymmetric bridging also contributes to the increase in the Co···Co separation.

The dihedral angle between the two O–Co–O planes of the [Co₂O₂] core is 157.6°. The sums of the angles around the oxygen atoms of the two phenolate oxygen bridges are 358.9 and 360.0° and demonstrate that a trigonal planar orientation is more pronounced. The O–Co–O angles

Table 1. Selected interatomic distances [Å] and angles for complexes **1**·dmf, **2**·CH₃OH, and **3**·CH₂Cl₂.^[a]

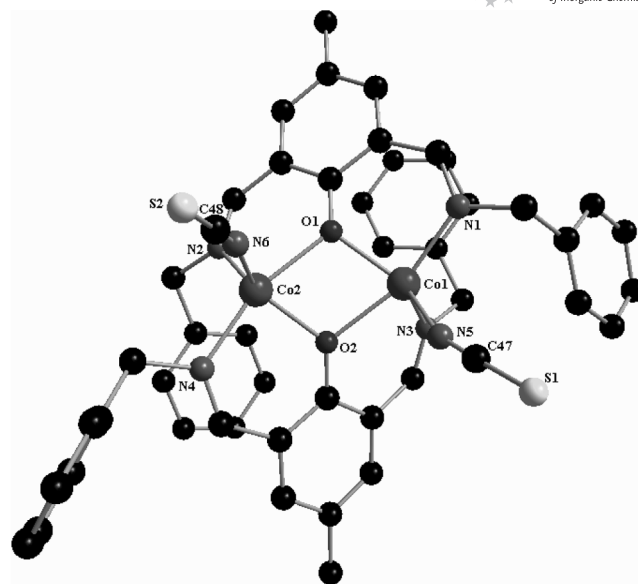
1·dmf			
Co1–O1	1.979(3)	Co2–O1	2.136(3)
Co1–O2	2.142(3)	Co2–O2	1.976(3)
Co1–N1	2.050(4)	Co2–N2	2.060(4)
Co1–N3	2.061(4)	Co2–N4	2.068(4)
Co1–N5	2.008(4)	Co2–N6	1.996(4)
Co1...Co2	3.2439(8)		
O1–Co1–O2	73.1(1)	O1–Co2–N2	84.9(1)
O1–Co1–N1	89.6(1)	O1–Co2–N4	162.5(1)
O1–Co1–N3	118.8(1)	O1–Co2–N6	91.0(2)
O1–Co1–N5	130.0(2)	O2–Co2–N2	118.4(1)
O2–Co1–N1	161.6(1)	O2–Co2–N4	89.8(2)
O2–Co1–N3	83.4(1)	O2–Co2–N6	125.3(2)
O2–Co1–N5	89.0(1)	N2–Co2–N4	107.6(2)
N1–Co1–N3	111.1(2)	N2–Co2–N6	111.6(2)
N1–Co1–N5	97.7(2)	N4–Co2–N6	95.4(2)
N3–Co1–N5	104.4(2)	Co1–O2–Co2	103.9(1)
Co1–O1–Co2	104.0(1)	Co1–N5–C47	163.2(4)
O1–Co2–O2	73.3(1)	Co2–N6–C48	162.8(4)

2·CH ₃ OH			
N2–Co1	2.067(2)	Co1–N1	2.058(2)
Co1–O1*	1.976(1)	Co1–O1	2.128(1)
Co1–N3	2.030(2)	Co1...Co1*	3.2541(8)
O1*–Co1–N3	136.94(8)	O1*–Co1–O1	72.30(6)
O1*–Co1–N1	118.39(6)	N3–Co1–O1	91.32(7)
N3–Co1–N1	98.05(8)	N1–Co1–O1	83.46(6)
O1*–Co1–N2	89.11(6)	N2–Co1–O1	158.39(6)
N3–Co1–N2	95.17(8)	Co1*–O1–Co1	104.89(6)
N1–Co1–N2	115.85(7)	N4–N3–Co1	126.4(2)

3·CH ₂ Cl ₂			
N2–Co1	2.070(4)	Co1–N1	2.087(4)
Co1–O1*	2.146(3)	Co1–O1	1.967(3)
Co1–N3	1.984(5)	Co1...Co1*	3.242(1)
O1*–Co1–N3	90.3(2)	O1*–Co1–O1	72.3(2)
O1*–Co1–N1	159.1(1)	N3–Co1–O1	133.4(2)
N3–Co1–N1	98.0(2)	N1–Co1–O1	88.3(1)
O1*–Co1–N2	83.4(1)	N2–Co1–O1	114.5(1)
N3–Co1–N2	105.6(2)	Co*–O1–Co1	104.0(1)
N1–Co1–N2	112.4(1)	C24–N3–Co1	171.6(5)

[a] *: 1 – x, y, 1/2 – z.

[73.1(2) and 73.3(1)°] within the [Co₂O₂] diamond core indicate considerable distortions at the metal ions. Two Co^{II} ions in distorted *tbp* polyhedra share the *basal-apical:apical-basal* (*b-a:a-b*) mode of binding (Scheme 2b). Two other alternative modes **1a** and **1c** are not observed. The values of the trigonality index, τ , of the two cobalt(II) centers are 0.52 and 0.61, respectively [where β represents the angles N1–Co1–O2 161.6(1)° and N4–Co2–O1 162.5(1)°; a represents O1–Co1–N5 130.0(2) and O2–Co2–N6 125.3(2)°].^[47] For an ideal value of β equal to 180° the corresponding τ values would have been 0.83 and 0.91. The equatorial plane consists of the one phenolate oxygen atom, one imine nitrogen atom of the other ligand, and the nitrogen end of the thiocyanate anion. The other imine nitrogen atom and the second bridging phenolate oxygen atom are in the *apical* positions. The angles around the Co^{II} center in the equatorial plane differ considerably from the ideal value of 120° [N3–Co1–O1 118.8(1), N3–Co1–N5 104.4(2), and N5–Co1–O1 130.0(2)°]. Bond lengths between Co^{II} and

Figure 1. Labeled ORTEP view of [Co₂(NCS)₂bip₂]·dmf (**1**·dmf) with atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level; H atoms are omitted for clarity.

the phenolate oxygen atoms vary significantly [Co1–O1 1.979(3) and Co1–O2 2.142(3) Å], with the shorter value corresponding to the *basal* binding. However, the *apical* distances do not fall in the usual range of average Co^{II}–O_{ph} distances observed in other pentacoordinate cobalt(II) complexes.^[19,42,45,46] The magnetically important Co–O–Co angles are 104.0(1) and 103.9(1)°. The Co^{II}–N_{im} distances are similar [Co1–N1 2.050(4), Co1–N3 2.061(4), Co2–N2 2.060(4), and Co2–N4 2.068(4)] and are close to the bond lengths observed in other pentacoordinate cobalt(II) complexes.^[42,43,45] The terminal Co–N_{NCS} distances are similar [Co1–N5 2.008(4) Å; Co2–N6 1.996(4) Å] and slightly shorter than the average Co–N_{im} distance.^[48] The thiocyanate terminal groups are almost linear, with N–C–S angles of 178.6(5) and 179.1(5)°. The nonlinear monodentate coordination of NCS[–] is reflected in the Co–N–C angles of 163.2(4) and 162.8(4)°.

The compound crystallizes with one disordered dimethylformamide solvent molecule, which is captured within the crystal lattice through C–H...O hydrogen bonds [C8...O1A ($x - 1, y, z - 1$) 3.15(1) Å and C8...O1B ($x - 1, y, z - 1$) 3.22(1) Å, for the two disordered moieties of dmf]. The crystal-packing diagram along the *a* axis show regular arrangement of isolated couples of **1** and dmf molecules without any other intermolecular short contacts (Supporting Information, Figure S2).

[Co^{II}(N₃)(bip)]₂·CH₃OH (2·CH₃OH)

The molecular structure of [Co^{II}(N₃)(bip)]₂ is shown in Figure 2 together with the atom labeling scheme used. A mononuclear Co^{II} fragment and 1/2 molecule of solvent methanol build up the crystallographic asymmetric unit. Complex **2**·CH₃OH is a Co^{II} dinuclear complex in the form of two fused distorted TBP of the [Co₂N₆O₂] core. The dinuclear aggregate is bridged and chelated by two ligands

in the same manner as in **1**, with the exception that N_3^- ions are more angularly bound to the cobalt(II) ions and the presence of one methanol molecule of crystallization. The structure consists of a $[\text{Co}^{\text{II}}(\text{N}_3)(\text{bip})]_2$ moiety that possesses a crystallographic twofold rotational axis of symmetry passing through the center of the $\text{Co1-O1-Co1}^*-\text{O1}^*$ ring (*: $1-x, y, 1/2-z$). Interestingly the value of the trigonality index, τ , of the cobalt(II) center is 0.35 [where β represents the angles N2-Co1-O1 $158.39(6)^\circ$; α represents $\text{O1}^*-\text{Co1-N3}$ $136.94(8)^\circ$], which is smaller than complex **1**.^[47] The $[\text{Co}_2\text{O}_2]$ unit [Co1-O1 $2.128(1)$ and $\text{Co1}^*-\text{O1}$ $1.976(1)$ Å] is formed from nonsymmetric *basal-apical* binding of two phenolate oxygen atoms with a separation of 3.25 Å (Supporting Information, Figure S3). The acute $\text{O}^*-\text{Co}-\text{O}$ angle of $72.30(6)^\circ$ within the $[\text{Co}_2\text{O}_2]$ core indicates a nonregular coordination site.

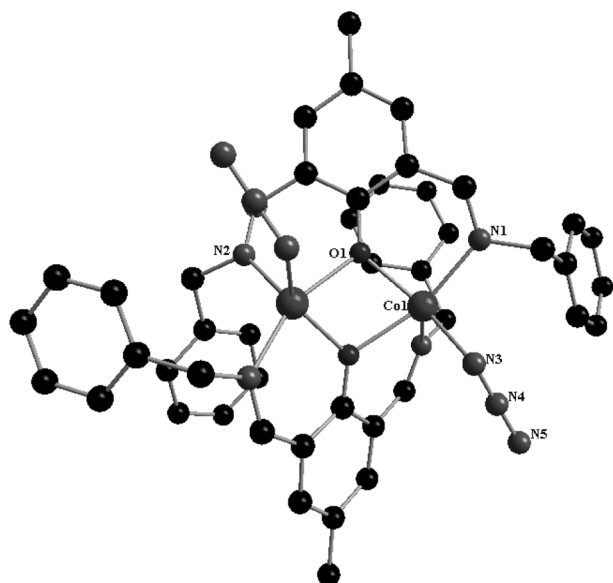


Figure 2. Labeled ORTEP view of $[\text{Co}_2(\text{N}_3)_2\text{bip}_2]\cdot\text{CH}_3\text{OH}$ (**2**· CH_3OH) with atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level; H atoms are omitted for clarity.

The Co-O-Co angle that contributes to the magnetic interactions is $104.89(6)^\circ$. The angles around the Co^{II} in the equatorial plane differ considerably from the ideal value of 120° [N3-Co1-N1 $98.05(8)$, N3-Co1-O1^* $136.94(8)$, and N1-Co1-O1^* $118.39(6)^\circ$]. The bond lengths between Co^{II} and the phenolate oxygen atoms vary significantly [Co1-O1^* $1.976(1)$ and Co1-O1 $2.128(1)$ Å], with the shorter value corresponding to the *basal* binding. However, the *apical* distances do not fall in the usual range of pentacoordinate $\text{Co}^{\text{II}}-\text{O}_{\text{ph}}$ distances. The $\text{Co}^{\text{II}}-\text{N}_{\text{im}}$ [Co1-N1 $2.058(2)$, Co1-N2 $2.067(2)$ Å] distances are similar and slightly longer than the $\text{Co}-\text{N}_{\text{N}_3}$ distances [Co1-N3 $2.030(2)$ Å].^[48] The azido terminal groups are almost linear with an N-N-N angle of $177.7(3)^\circ$. The N_3^- groups show nonlinear monodentate terminal binding and a smaller Co-N-N angle [$126.4(2)^\circ$] than that of NCS^- in previous molecules. In the crystal packing, it is worth mentioning that no signifi-

cant H-bonding network is observed. A crystal-packing diagram along the c axis is shown in the Supporting Information (Figure S4).

$[\text{Co}^{\text{II}}(\text{NCO})(\text{bip})]_2\cdot\text{CH}_2\text{Cl}_2$ (**3**· CH_2Cl_2)

The ORTEP view of $[\text{Co}^{\text{II}}(\text{NCO})(\text{bip})]_2$ is shown in Figure 3 together with the atom labeling scheme used. The last member (i.e., **3**) of this series of compounds is obtained by binding of one NCO^- to each of the Co^{II} ions in a similar manner with one dichloromethane molecule of crystallization. The asymmetric *basal-apical* bridging by two phenolate oxygen atoms leads to a $\text{Co}\cdots\text{Co}$ separation of 3.24 Å (Supporting Information, Figure S5). The value of the trigonality index, τ , of the cobalt(II) center is 0.42 [where β represents the angles N1-Co1-O1^* $159.1(1)^\circ$; α represents O1-Co1-N3 $133.4(2)^\circ$], which is smaller than complex **1** but bigger than complex **2**.^[47]

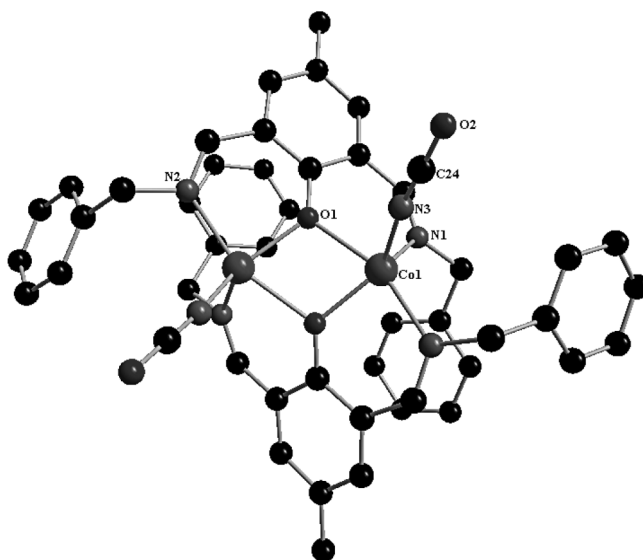


Figure 3. Labeled ORTEP view of $[\text{Co}_2(\text{NCO})_2\text{bip}_2]\cdot\text{CH}_2\text{Cl}_2$ (**3**· CH_2Cl_2) with atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level; H atoms are omitted for clarity.

The angles around Co^{II} in the equatorial plane differ considerably from the ideal value of 120° [N3-Co1-O1 $133.4(2)$, N2-Co1-O1 $114.5(1)$, and N2-Co1-N3 $105.6(2)^\circ$]. The Co-O-Co angle is $104.0(1)$. The cyanato terminal groups are almost linear with an N-C-O angle of $178.1(8)^\circ$. The NCO^- groups like NCS^- and N_3^- show typical terminal binding and a greater Co-N-C angle [$171.6(5)^\circ$] compared to NCS^- and N_3^- in the previous two structures. As in the two other complexes, no H-bonding network is seen in the crystal packing (shown along the b axis in Figure S6 in the Supporting Information).

The Role of the N-Benzyl Groups of Ligands in Molecular Distortions

The pendant benzyl groups of the ligands are responsible for the noncoplanar placement of the two bip^- ligands around two *hs* Co^{II} ions. The two Co^{II} ions lie in a distorted

pentacoordination environment defined by three N- and two O-donor atoms from the two ligands and two pseudohalides. The best mean planes of two coordinated ligands excluding the N-benzyl groups in three structures are inclined at an angle ranging from 54.36 to 63.06° (Figure 4; Supporting Information, Figure S7). In the presence of one bound pseudohalide to each Co^{II} this arrangement of the ligands favor highly distorted coordination geometry and control the $\text{Co}^{\text{II}}\cdots\text{Co}^{\text{II}}$ separations and $\text{Co}^{\text{II}}\text{--O--Co}^{\text{II}}$ bridge angles.

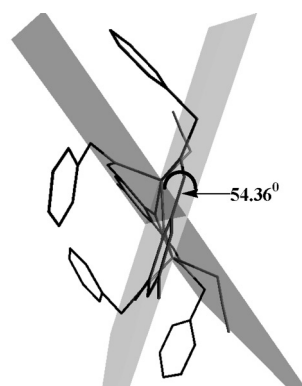


Figure 4. Nonplanar orientations of ligands showing the inclination of the mean planes of two coordinated ligands excluding the N-benzyl groups in **1**-dmf.

A nonsymmetric *basal–apical* bridge from the phenolate oxygen atoms further stabilizes the distorted geometries. This bridge is responsible for the change in metal–metal separations and metal–oxygen–metal angles, as *apical* binding always leads to out-of-plane longer bonds, which is most common in azido-bridged Cu^{II} systems (Scheme 2).^[49] Interestingly with a similar dioxime-based ligand Hdox (Scheme 1) the dinuclear complex of Co^{II} exhibits a nearly planar structure in which each metal center adopts an octahedral coordination geometry and *basal–basal* binding.^[36] The two Co^{II} ions lie in a plane defined by four N- and two O-donor atoms from the two ligands.

Spontaneous Dimerization for Unsymmetrical Phenolate *basal–apical* (b–a) and *apical–basal* (a–b) Bridges

Recently, we reported the coordination behavior of Hdfp as a bridging coligand in the symmetrical *basal–basal* mode of binding to octahedral *hs* Co^{II} ions.^[14] The Co–O distances were 2.085 and 2.057 Å within the $\text{Co}^{\text{II}}_2(\text{dfp})$ fragment. Herein the dihedral angles between the two chelate rings of bip^- in the three complexes are 156.8, 155.8, and 154.8° as compared to 163.0° observed in the case of dfp^- binding (Figure 5).^[14,50]

The bidentate N,O chelation from one half of the first bip^- ligand to Co^{II} and binding of one A^- (NCS^- , N_3^- , or NCO^-) and two solvent molecules yield the electroneutral intermediate I (Scheme 4). Interaction toward dimerization of two such species takes place through the interactions from dangling imine nitrogen atoms from a second bip^- ligand and produces intermediate II. In the next step,

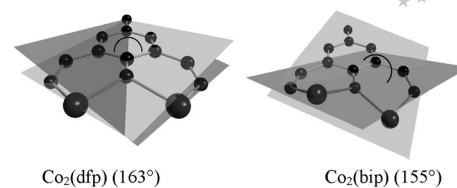


Figure 5. Angle between the chelate rings of bip^- and dfp^- .

bridging interactions from the phenolate groups in the *basal–apical* mode result in intermediate III, which finally separates **1–3** from the reaction mixture. A similar type of aggregation reaction of two trinuclear fragments into a hexanuclear unit was described by us for a Ni^{II}_6 complex.^[51]

Magnetic Properties

The solid-state magnetic properties of **1**-dmf, **2**- CH_3OH , and **3**- CH_2Cl_2 were investigated by using dc susceptibility measurements in the temperature range 1.8–300 K in a 1 T magnetic field (Supporting Information, Figure S8). The data reported in Figure 6 were plotted as χT vs. T . At room temperature, the χT products are 4.1, 4.9, and 4.5 $\text{cm}^3 \text{K mol}^{-1}$ for **1**-dmf, **2**- CH_3OH , and **3**- CH_2Cl_2 , respectively.

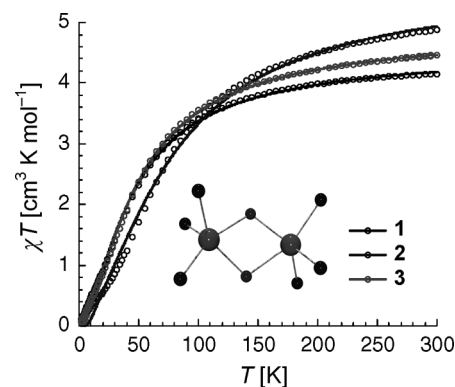


Figure 6. Plot of χT vs. T per mol of **1**-dmf, **2**- CH_3OH , and **3**- CH_2Cl_2 (where χ is defined as M/H per dinuclear Co^{II} complex). The solid lines are the best fit obtained by using the isotropic dinuclear $S = 3/2$ Heisenberg model described in the text. The inset is a scheme of the core of **1–3**.

The values of χT are in reasonably good agreement with the theoretical value of 3.75 $\text{cm}^3 \text{K mol}^{-1}$, which is expected for two isolated paramagnetic *hs* Co^{2+} ions (d^7 , $S = 3/2$) with $g = 2$. The fact that the observed χT products are slightly higher than the theoretical value, indicating a g factor higher than 2, is likely due to the effects of the magnetic anisotropy associated with each *hs* Co^{2+} ion. Upon cooling, both χT products continuously decrease for all compounds, indicating that dominant antiferromagnetic exchange interactions exist between the two Co^{2+} ions of the dinuclear complexes. At 1.8 K and under 1 T, the χT product reaches 0.10, 0.10, and 0.07 $\text{cm}^3 \text{K mol}^{-1}$, as expected when intramolecular antiferromagnetic interactions dominates to lead here to a singlet ground state ($S_T = 0$). Below ca. 50 K, there may also be the additional contributions of intermo-

molecular antiferromagnetic interactions and/or second-order spin–orbit coupling associated with the distorted pentacoordinate site symmetry at each Co^{2+} metal ion center.^[52] The susceptibility of such Co^{II} complexes are usually not theoretically reproducible, as no analytical expression that includes intramolecular magnetic interaction and second-order spin–orbit couplings can be easily used. Nevertheless, the general shape and trend of the χT vs. T plots for **1**·dmf, **2**·CH₃OH, and **3**·CH₂Cl₂ (Figure 6) are similar to that reported for another structurally related dinuclear, pentacoordinate *hs* Co^{II} complex, with distorted SP site symmetry at each of the Co^{2+} metal ion centers.^[22] Lastly, there is an additional slight deviation of the χT value for **1**·dmf and **3**·CH₂Cl₂ below ca. 30 K at low fields (typically 1000 Oe), indicating the presence of a trace amount of byproducts that display a magnetic order in the measured samples (this byproduct is also seen in the χ vs. T data, Figure S8 in the Supporting Information, and the M vs. H data that display a tiny but typical *S*-shape curve around zero field). Such magnetic impurities cannot be easily corrected for, but their effect on the magnetic data of the major compound is minimized at 1 T (it was checked for all compounds that the M vs. H plot at 1 T is still linear; i.e., in the low field or Curie limit). Thus, for the purposes of modeling the χT data only, the data collected at 1 T were used for the fit. On the basis of the structure, the complex can be topologically viewed as a spin dimer composed of two $S = 3/2$ Co^{II} ions. The single-crystal X-ray structures of these compounds reveal a distorted SP ligand field at each Co^{II} ion that should not exhibit any first-order spin–orbit coupling in idealized C_{4v} site symmetry, as the degeneracy of the occupied d_{xy}, xz, zy orbitals is lifted. Thus, this effect should be small and the magnetic data were approximately modeled by using an isotropic Heisenberg spin Hamiltonian to estimate the value of the exchange interaction:

$$H = -4J\{S_{\text{Co},1} \cdot S_{\text{Co},2}\}$$

where J is the exchange interactions within the [Co^{II}_2] complex; S_i the spin operators for each spin carriers. The application of the van Vleck equation^[53] to the Kambe's vector coupling scheme^[54] allows a determination of the low-field analytical expression of the magnetic susceptibility:^[55]

$$\chi T = \frac{N\mu_B^2 g_{\text{Co}}^2}{k_B} \frac{2e^{\frac{2J}{k_B T}} + 10e^{\frac{6J}{k_B T}} + 28e^{\frac{12J}{k_B T}}}{1 + 3e^{\frac{2J}{k_B T}} + 5e^{\frac{6J}{k_B T}} + 7e^{\frac{12J}{k_B T}}}$$

As seen in Figure 6, this model was able to reproduce well the experimental χT vs. T data from 300 to 1.8 K. The best set of parameters obtained by using the above model are $J/k_B = -10.6(4)$ K and $g = 2.21(4)$ for **1**·dmf, $J/k_B = -18.1(7)$ K and $g = 2.49(2)$ for **2**·CH₃OH, and $J/k_B = -11.6(3)$ K and $g = 2.30(3)$ for **3**·CH₂Cl₂. It is worth mentioning that the obtained parameters must be taken with caution due to the likely presence of second-order spin–orbit effects that have not been taken into account in this model. The J parameters might thus be slightly overestimated as they could contain phenomenologically other

magnetic effects like the intermolecular antiferromagnetic interactions or magnetic anisotropy. Indeed, these effects might explain the lower quality of the fit for **2**·CH₃OH that possesses the higher g value of the series and thus probably the larger spin–orbit coupling. Therefore, it is difficult to further analyze the magnetic data and make an accurate correlation between the geometry of the Co–O₂–Co bridge and the obtained magnetic interactions. This point is reinforced by the fact that, as far as we know, no other complex displays similar geometry with Co–O bond lengths of about 1.97–1.98 Å and 2.13–2.15 Å in order to directly correlate the Co–O–Co angles with the interaction parameter. Nevertheless, a relatively good linearity is found plotting J as a function of the average Co–O–Co giving: $J(\text{K}) = 824 - 8 \theta(^{\circ})$ (Supporting Information, Figure S9). It is worth emphasizing that this linear relation must be considered with caution and will have to be confirmed by the magnetic properties of future dinuclear Co^{II} complexes of the same geometry.

Concluding Remarks

In summary, the [Co^{II}_2] nuclearity in the form of two shared and distorted square-pyramids, in a new family containing three different pseudohalide anions, was achieved by the combined action of coordinations of three different pseudohalide anions and a pendant benzyl group bearing the Schiff base ligand anion *bip*[−]. These coordinations introduce a pair of complementary *basal*–*apical* phenolate bridges that cause, within these [Co^{II}_2] assemblies, weak intramolecular antiferromagnetic interactions. Binding of a single pseudohalide anion to each *hs* Co^{II} ion is responsible for the nonplanar orientation of the two ligands, ensuing in distortions of the coordination geometries remarkable in synthesis but familiar in biology. We are currently working to exploit other bridging groups in this reaction system in order to induce the formation of heterometallic binuclear and high nuclearity complexes.

Experimental Section

Materials and Physical Measurements: Ammonium thiocyanate, sodium azide, triethylamine, and cobalt acetate tetrahydrate were obtained from SRL Chem. (India). Sodium cyanate was obtained from Lancaster (England). 2,6-Bis(benzyliminomethyl)-4-methylphenolate (Hbip) was prepared by a literature procedure.^[34] All other chemicals and solvents were reagent grade materials and were used as received without further purification. Microanalyses were performed by using a Perkin–Elmer model 2400 microanalyzer. FTIR spectra were recorded with a Perkin–Elmer RX1 spectrometer. The solution electrical conductivity and electronic spectra were obtained by using a Unitech type U131C digital conductivity meter with a solute concentration of about 10^{-3} M and a Shimadzu 1601 UV/Vis/NIR spectrophotometer, respectively. ¹H and ¹³C NMR spectra were recorded in CDCl₃ with a Bruker AC 200 NMR spectrometer by using TMS as the internal standard. The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL housed at the Centre de Recherche Paul Pascal. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from −7 to 7 T. Mea-

measurements were performed on polycrystalline samples of 14.86, 11.00, and 10.67 mg, for **1**·dmf, **2**·CH₃OH, and **3**·CH₂Cl₂, respectively. The magnetic data were corrected for the sample holder and diamagnetic contributions. All experimental procedures were carried out in air at room temperature.

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

[Co^{II}₂(NCS)₂(bip)₂](dmf) (1·dmf): To a solution of the ligand (0.342 g, 1.00 mmol) in methanol (15 mL) was added a solution of Co(OAc)₂·4H₂O (0.498 g, 2.00 mmol) in methanol (20 mL), followed by the dropwise addition of a solution of NH₄SCN (0.304 g, 4.00 mmol) in methanol (15 mL), and the mixture was stirred at ambient temperature in air. After 15 min, NEt₃ (0.14 mL, 1.00 mmol) was added, and the reaction mixture was stirred for 1 h. After evaporation of the reaction mixture, a pale-green solid was obtained. The solid was isolated, washed with cold methanol, and dried under vacuum over P₄O₁₀. Single crystals suitable for X-ray analysis were obtained from dmf after 10 d. Yield: 0.344 g (75%). C₅₁H₄₉Co₂N₇O₃S₂ (989.9921): calcd. C 61.87, H 4.98, N 9.90; found C 61.79, H 4.87, N 9.64. FTIR (KBr): $\tilde{\nu}$ = 3447 (vs), 2071 (vs), 1628 (vs), 1558 (vs), 1341 (m), 707 (m) cm⁻¹. Molar conductance (dmf): Λ_M = 4 Ω^{-1} cm² mol⁻¹. UV/Vis (dmf): λ (ϵ , M⁻¹ cm⁻¹) = 578 (199), 398 (7360), 326 (8590), 250 (23870) nm.

[Co^{II}₂(N₃)₂(bip)₂](CH₃OH) (2·CH₃OH): Prepared by the same method as that used for **1** by replacing NH₄SCN with NaN₃. Single crystals suitable for X-ray analysis were obtained from a dcm/MeOH mixture after 4 d. Yield: 0.345 g (78%). C₄₇H₄₆Co₂N₁₀O₃ (916.8134): calcd. C 61.57, H 5.05, N 15.27; found C 61.49, H 4.94, N 15.01. FTIR (KBr): $\tilde{\nu}$ = 3447 (vs), 2050 (vs), 1627 (vs), 1551 (vs), 1345 (m), 705 (m) cm⁻¹. Molar conductance (dcm): Λ_M = 6 Ω^{-1} cm² mol⁻¹. UV/Vis (CH₂Cl₂): λ (ϵ , M⁻¹ cm⁻¹) = 578 (439), 398 (3683), 326 (4016), 252 (14787) nm.

[Co^{II}₂(NCO)₂(bip)₂](CH₂Cl₂) (3·CH₂Cl₂): Prepared by the same method as that used for **1** by using NaNCO instead of NH₄SCN. Single crystals suitable for X-ray analysis were obtained from a dcm/MeOH mixture after 5 d. Yield: 0.318 g (72%). C₄₉H₄₄Cl₂Co₂N₆O₄ (969.6966): calcd. C 60.69, H 4.57, N 8.66; found C 60.61, H 4.46, N 8.41. FTIR (KBr): $\tilde{\nu}$ = 3448 (vs), 2207 (vs), 1629 (vs), 1552 (vs), 1345 (m), 705 (m) cm⁻¹. Molar conductance (dcm): Λ_M = 5 Ω^{-1} cm² mol⁻¹. UV/Vis (CH₂Cl₂): λ (ϵ , M⁻¹ cm⁻¹) = 581 (291), 400 (6721), 327 (4213), 251 (21692) nm.

X-ray Crystallographic Procedures for 1·dmf, 2·CH₃OH, and 3·CH₂Cl₂: The intensity data of complexes **2** and **3** were collected on single crystals by using a Bruker-APEX-2 X-ray diffractometer equipped with graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å) by the hemisphere method. Data were collected at 293 K. The intensity data of complex **1** was collected with a Nonius Kappa CCD diffractometer by using graphite monochromated Mo-*K*_α radiation (λ = 0.7107 Å) at low temperature (120 K). Information concerning X-ray data collection and structure refinement of the compound is summarized in Table 2. 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 a riding model. In compound **1**·dmf, the dmf molecule was found to be disordered and its HC=O moiety was refined over two positions with an occupancy of 0.5 each. In compound **2**·CH₃OH, the CH₃OH solvent molecule is disordered across a center of symmetry and was refined with an occupancy of 0.5. The corresponding hydrogen atoms could not be determined. In compound **3**·CH₂Cl₂, the CH₂Cl₂ solvent molecule is situated on a twofold axis, displays some disorder, and was refined anisotropically. The corresponding hydrogen atoms could not be determined. The structures were solved by direct methods (SIR97)^[56] All other calculations were performed by using SHELXL-97^[57] and PARST^[58] implemented in WINGX system of programs.^[59] CCDC-707903 (for **1**·dmf),

Table 2. Crystallographic data for **1**·dmf, **2**·CH₃OH, and **3**·CH₂Cl₂.

	1 ·dmf	2 ·CH ₃ OH	3 ·CH ₂ Cl ₂
Formula	C ₅₁ H ₄₉ Co ₂ N ₇ O ₃ S ₂	C ₄₇ H ₄₆ Co ₂ N ₁₀ O ₃	C ₄₉ H ₄₄ Co ₂ N ₆ O ₄ Cl ₂
<i>M</i>	989.9921	916.8134	969.6966
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
Crystal system	monoclinic	monoclinic	monoclinic
<i>a</i> [Å]	10.7411(2)	22.131(5)	19.215(5)
<i>b</i> [Å]	28.5248(5)	11.689(3)	22.901(6)
<i>c</i> [Å]	15.1638(3)	17.061(4)	12.682(3)
β [°]	94.3202(8)	93.688(6)	124.737(6)
<i>V</i> [Å ³]	4632.80(15)	4404.4(17)	4586(2)
<i>T</i> [K]	120	293	293
<i>Z</i>	4	4	4
<i>D</i> _c [g cm ⁻³]	1.419	1.383	1.404
<i>F</i> (000)	2056	1904	2000
μ (Mo- <i>K</i> _α) [cm ⁻¹]	8.58	8.07	8.91
Measured reflns.	34170	29677	24506
Unique reflns.	8973	5207	4021
<i>R</i> _{int}	0.0779	0.0354	0.0424
Obsd. reflns. [<i>I</i> ≥ 2σ(<i>I</i>)]	6061	3841	2699
$\theta_{\min}$ – $\theta_{\max}$ [°]	2.25–26.00	1.84–28.00	1.78–25.00
<i>hkl</i> ranges	–13, 13; –35, 34; –18, 18	–29, 29; –15, 14; –20, 20	–22, 22; –27, 23; –14, 15
<i>R</i> (<i>F</i> ²) (obsd. reflns.)	0.0662	0.0373	0.0511
<i>wR</i> (<i>F</i> ²) (all reflns.)	0.1707	0.1101	0.1699
No. variables	588	280	286
Goodness of fit	1.031	1.025	1.056
$\Delta\rho_{\max}$; $\Delta\rho_{\min}$ [e Å ⁻³]	1.61; –0.53	0.50; –0.309	0.733; –0.467

-707904 (for $2\cdot\text{CH}_3\text{OH}$), and -707905 (for $3\cdot\text{CH}_2\text{Cl}_2$) 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 footnote on the first page of this article): ORTEP representations and packing diagrams of $1\cdot\text{dmf}$, $2\cdot\text{CH}_3\text{OH}$, and $3\cdot\text{CH}_2\text{Cl}_2$; Space-filling diagram of $1\cdot\text{dmf}$; plot of χ vs. T per mole of $1\cdot\text{dmf}$, $2\cdot\text{CH}_3\text{OH}$, and $3\cdot\text{CH}_2\text{Cl}_2$; magnetostuctural correlation between J and the average Co–O–Co angle.

Acknowledgments

M. S. is thankful to the Council of Scientific and Industrial Research, New Delhi, for financial support. V. B. acknowledges the Italian Ministry of University and Scientific Research (MIUR, Rome). R. C., C. M., and N. G. R. H. thank the University of Bordeaux, the Centre National de la Recherche Scientifique (CNRS), the Region Aquitaine, and Molecular Approach to Nanomagnets and Multifunctional Materials, Network of Excellence (MAG-MANet) (NMP3-CT-2005-515767) for funding. N. G. R. H. also thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for a postdoctoral fellowship.

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Received: June 23, 2009

Published Online: September 21, 2009