Six-coordinate Co^{III} and four-coordinate M^{II} (M = Co, Zn) mixed-valence dimers supported by a deprotonated pyridine amide ligand: magnetism of a $Co^{III}Co^{II}$ complex and C–H···O/Cl/Br interactions†

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Received (in Montpellier, France) 19th August 2008, Accepted 14th January 2009
First published as an Advance Article on the web 24th February 2009
DOI: 10.1039/b814303j

Using a pyridine amide ligand 4-methyl-2-{*N*-(2-pyridyl)carbamoyl}pyridine (HL), in its deprotonated form, binuclear mixed-valence homonuclear bimetallic complexes $[Co^{III,II}_2(L)_3(X)]X\cdot S$ [X = Cl (**1**); X = Br, S = CH_3OH (**2**)] and heteronuclear bimetallic complex $[Co^{III}Zn^{II}(L)_3(Cl)]Cl\cdot CH_3OH\cdot 5H_2O$ (**3**) have been synthesized. Structural analysis revealed that trivalent cobalt is in distorted octahedral and bivalent cobalt/zinc is in distorted tetrahedral environment. Three L(−) ligands provide six-coordination by utilizing three pyridine amide units (pyridine N and amide N donor set) in a facial mode, which in turn places three 4-methylpyridine nitrogens to coordinate to another metal center, which completes four-coordination by a chloride/bromide ion. Temperature-dependent magnetic susceptibility measurements in the solid state of a representative complex **1** revealed the spin-states as Co^{III} ($S = 0$) and Co^{II} ($S = 3/2$), with a zero-field splitting parameter for Co^{II} ($g = 2.20$ and $D = 3.9\ cm^{-1}$; $2D$ is the energy gap between the two Kramers doublets $M_s = |\pm 3/2\rangle$ and $|\pm 1/2\rangle$). To the best of our knowledge, this is for the first time that a pyridine amide ligand has been utilized to accommodate two cobalt ions or a cobalt and a zinc ion in different geometry, oxidation state, and spin-state (class I mixed-valence dimer). The crystal packing diagram reveals interesting non-covalent interactions involving C–H···O/Cl/Br, leading to the generation of 1D, 2D and 3D supramolecular architectures. Absorption spectral and redox properties of the complexes have also been investigated.

Introduction

There has been continued interest in the development of coordination chemistry of peptide ligands containing the pyridine-2-carboxamide[1–5] and pyridine-2,6-dicarboxamide[1,6–8] functionality in deprotonated form. Many such complexes act as bioinorganic models[9] and catalysts for selective organic transformations.[4j,k,10] From the standpoint of exploring coordination chemistry of deprotonated pyridine amide ligands we[2,6] and others[3–5,7,8] have synthesized, structurally characterized and investigated properties of a large variety of interesting transition metal complexes.

Herein we examine the coordination ability of HL primarily towards cobalt, anticipating that as a result of chelate-ring constraints the deprotonated ligand L(−) with three donor sites will coordinate to two metal ions. We reasoned that three L(−) units utilizing pyridine-2-carboxamide units would support a six-coordinate Co^{III} ion and such a situation in turn would place three pyridine nitrogens of the 4-methyl-2-aminopyridine units in a facial arrangement to hold another metal ion Co^{II} or Zn^{II}. The fourth coordination site around Co^{II} or Zn^{II} could be completed by a chloride or bromide ion originating from the cobalt(II) starting material. Very facile formation of mixed-valence $Co^{III}Co^{II}$ complexes indeed occurs in the aerobic reaction of L^- (HL + K_2CO_3) with cobalt(II) chloride/bromide tetrahydrate, in molar ratio 2 : 3, as potential supporter of this situation. Our realization has been authenticated by structural analysis of $[Co^{III}Co^{II}(L)_3(Cl)]Cl$ (**1**), $[Co^{III}Co^{II}(L)_3(Br)]Br\cdot CH_3OH$ (**2**) and $[Co^{III}Zn^{II}(L)_3(Cl)]Cl\cdot CH_3OH\cdot 5H_2O$ (**3**). Temperature-dependent magnetic susceptibility measurements for **1** in the solid-state revealed the spin-states as Co^{III} ($S = 0$) and Co^{II} ($S = 3/2$). To the best of our knowledge, **1** and **2** represent the first structural proof[11] of discrete homonuclear bimetallic mixed-valence[12] complexes with two cobalt centers differing in geometry, oxidation state (a six-coordinate Co^{III} and a four-coordinate Co^{II}) and spin state, supported by a deprotonated pyridine amide ligand.

As part of our activity[13] in inorganic crystal engineering[14] we became interested in the investigation of non-covalent interactions in the complexes **1–3**. A closer scrutiny of the X-ray structural packing diagrams reveals interesting

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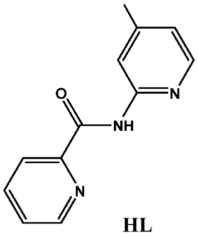
† Electronic supplementary information (ESI) available: Fig. S1–13: Supplementary Figures showing ^1H NMR, UV-vis, magnetic data and cyclic voltammogram for **1** and crystal packing diagrams for **1–3**. CCDC reference numbers 639424 (**1**), 698530 (**2**) and 698531 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814303j

noncovalent interactions involving C–H···O/Cl/Br, leading to the generation of 1D, 2D and 3D supramolecular architectures. Electronic spectral and redox properties of the complexes have also been investigated.



HL

Results and discussion

Synthesis and general characterization

The new ligand 4-methyl-2-{*N*-(2-pyridyl)carbamoyl}pyridine (HL) was prepared in high yield (adapted from reported procedures)[15] by treating pyridine-2-carboxylic acid with 2-amino-4-methylpyridine in the presence of triphenylphosphite, as water scavenger. It should be mentioned here that the ligand HL without methyl substituent in the 2-aminopyridine ring is reported in the literature.[4n,15a] It is of note here that a series of mononuclear transition metal bis-ligand complexes of the 2-{*N*-(2-pyridyl)-carbamoyl}pyridine ligand (without methyl substituent) in its neutral form have been reported. In all the reported complexes the ligand acts as a bidentate ligand with one uncoordinated pyridine ring.[4n,15a] We deliberately synthesized a methyl substituted analogue of the reported ligand to enhance the donor property of the 2-aminopyridine moiety of the ligand so that the modified ligand can act as a binucleating ligand. The designed synthesis of the homonuclear bimetallic complexes $[Co^{III,II}_2(L)_3(Cl)]Cl$ (**1**) and $[Co^{III,II}_2(L)_3(Br)]Br{\cdot}CH_3OH$ (**2**) is based on the following considerations: (i) L(−) acts as a binucleating ligand, with potential to utilize its 4-methylpyridine nitrogen for coordination to a second metal ion, (ii) L(−) can assume different coordination modes and the one to be adopted in a complex formation is governed by the reaction conditions[4n,15a] and (iii) the Co^{III} ion coordinated by deprotonated pyridine amide ligands in a six-coordinate geometry is expected to be in the low-spin state[2a,6d] and the Co^{II} ion is expected to be in four-coordinate geometry with the given combination of deprotonated HL and a Cl^-/Br^- ion. For a generalization of our expectation we decided to synthesize a heteronuclear bimetallic complex $[Co^{III}Zn^{II}(L)_3(Cl)]Cl{\cdot}CH_3OH{\cdot}5H_2O$ (**3**). Keeping these points in mind we set out to synthesize the complexes. The reaction stoichiometry, behind the successful synthesis of complexes, could be presented in eqn (1) (synthesis of **1** and **2**) and eqn (2) (synthesis of **3**).

$$\begin{aligned}&4Co^{II}X_2{\cdot}4H_2O + 6HL + 2K_2CO_3 + 1/2O_2\\&\rightarrow 2[Co^{III}Co^{II}(L)_3(X)]^+X^- + 4KX + 19H_2O\\&\quad(X = Cl \text{ or } Br) + 2CO_2 \qquad (1)\end{aligned}$$

$$\begin{aligned}&2Co^{II}Cl_2{\cdot}4H_2O + 6HL + 2K_2CO_3 + 2ZnCl_2 + 1/2O_2\\&\rightarrow 2[Co^{III}Zn^{II}(L)_3(Cl)]^+Cl^- + 4KCl + 11H_2O + 2CO_2\\&\qquad (2)\end{aligned}$$

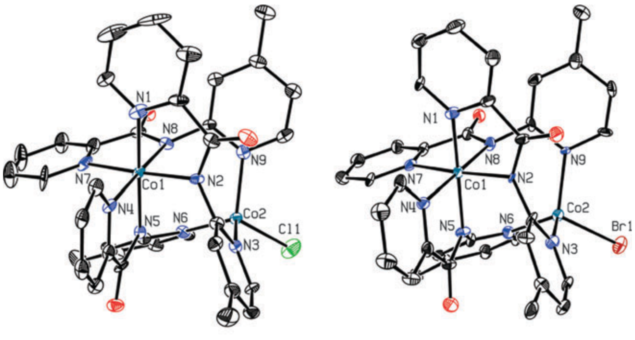
The air-stable complexes **1** (blue), **2** (violet-blue) and **3** (pink) were isolated in a reasonable yield (∼60%). All the complexes **1**, **2** and **3** are soluble in common organic solvents such as CH_2Cl_2, CH_3CN and DMF. Elemental analysis, IR (absence of –NH vibration indicates coordination by the deprotonated ligand; broad absorption at ∼3400 cm^{-1} is observed due to ν_{OH} of CH_3OH molecule present in **2** and of CH_3OH and water molecules present in **3** as solvent of crystallization) and solution electrical conductivity data of **1** (1 : 1 electrolyte in CH_3CN)[16] are in excellent agreement with the above formulation of the new complex. The structures of all three complexes **1**, **2** and **3** have been authenticated by X-ray crystallography (*vide infra*).

The data (in CD_3CN) of the heterobinuclear Co^{III} low-spin (d^6) and Zn^{II} (d^{10}) diamagnetic complex $[Co^{III}Zn^{II}(L)_3(Cl)]Cl{\cdot}CH_3OH{\cdot}5H_2O$ (**3**), along with their assignments are recorded in the Experimental section (Fig. S1, ESI†). It supports the expected structure, authenticated by X-ray structure analysis (see below) [three L(−) ligands are coordinated to a grossly octahedral Co^{III} ion and a grossly tetrahedral Zn^{II} ion]. The proton resonances were assigned based on the available ^1H NMR spectral data of the free ligand HL.[4n,13a] The following comments regarding the spectral data are in order. (i) All three ligands are chemically/magnetically equivalent, displaying only one signal for a given proton. (ii) The ring proton resonances for pyridine ring coordinated to Co^{III} are downfield shifted compared to that for the ring proton resonances for pyridine ring coordinated to Zn^{II}. This implies the presence of more electron density at the 4-methyl-2-aminopyridine ring. This is understandable as the pyridine ring coordinated to the Co^{III} ion is expected to donate more electron density to the metal ion, compared to the pyridine ring coordinated to Zn^{II} ion. Moreover, the 4-methyl-2-aminopyridine ring has an electron-releasing methyl substituent. In essence, the ^1H NMR results of **3** clearly indicate that the solid-state structures (*vide infra*) are retained in solution.

The absorption spectrum of complexes **1**, **2** and **3** were recorded in CH_3CN in the range 220–1100 nm. The case of **1** is displayed in Fig. S2 (ESI†). All three complexes display an absorption band around 550 nm which is assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ transition, associated with low-spin Co^{III} in octahedral parentage.[2a,6d,17] The complexes **1** and **2** display a crystal-field absorption at ∼1000 nm (precise peak position could not be made due to limitations associated with available spectrophotometer) due to $^4A_2 \rightarrow {}^4T_1(F)$ transition, associated with Co^{II} in tetrahedral parentage.[17] Still higher energy transitions are due to charge-transfer origin.

Structural considerations

Crystal structures of $[Co^{III,II}_2(L)_3(X)]X{\cdot}S$ [X = Cl (1); X = Br, S = CH_3OH (2)]. Perspective views of the cations in $[Co^{III,II}_2(L)_3(Cl)]Cl$ (**1**) and $[Co^{III,II}_2(L)_3(Br)]Br{\cdot}CH_3OH$ (**2**) are displayed in Fig. 1 and selected bond distances and angles are collected in Table 1. The asymmetric unit of **2** contains two crystallographically independent molecules. In both the complexes three L(−) ligands are coordinated to two cobalt ions, one in grossly octahedral and the other in grossly tetrahedral geometry. Three pyridine-2-carboxamido nitrogens from three L(−) are coordinated to the Co(1) center in a facial



(a) (b)

Fig. 1 View of (a) $[\mathrm{Co^{III,II}}_2(\mathrm{L})_3(\mathrm{Cl})]^+$ in the structure of $[\mathrm{Co^{III,II}}_2(\mathrm{L})_3(\mathrm{Cl})]\mathrm{Cl}$ (**1**) and (b) $[\mathrm{Co^{III,II}}_2(\mathrm{L})_3(\mathrm{Br})]^+$ in the structure of $[\mathrm{Co^{III,II}}_2(\mathrm{L})_3(\mathrm{Br})]\mathrm{Br}\cdot\mathrm{CH_3OH}$ (**2**) with 30% probability. Hydrogen atoms are omitted for clarity.

Table 1 Selected bond distances (Å) and angles (°) in $[\mathrm{Co^{III,II}}_2(\mathrm{L})_3(\mathrm{Cl})]\mathrm{Cl}$ (**1**) and $[\mathrm{Co^{III,II}}_2(\mathrm{L})_3(\mathrm{Br})]\mathrm{Br}\cdot\mathrm{CH_3OH}$ (**2**)

	1	**2**
Co(1)–N(1)	1.936(5)	1.953(6) [1.959(8)]
Co(1)–N(2)	1.941(5)	1.955(5) [1.944(7)]
Co(1)–N(4)	1.949(4)	1.962(6) [1.947(9)]
Co(1)–N(5)	1.934(5)	1.959(6) [1.942(7)]
Co(1)–N(7)	1.937(5)	1.944(5) [1.952(7)]
Co(1)–N(8)	1.961(4)	1.971(6) [1.945(7)]
Co(2)–N(3)	2.026(5)	2.058(6) [2.030(6)]
Co(2)–N(6)	2.011(5)	2.027(6) [1.998(6)]
Co(2)–N(9)	2.019(5)	2.014(5) [2.029(7)]
Co(2)–Cl(1)/Br(1)	2.226(2)	2.3752(14) [2.3694(15)]
N(1)–Co(1)–N(2)	82.8(2)	83.4(2) [83.2(3)]
N(1)–Co(1)–N(4)	95.8(2)	93.4(2) [97.2(4)]
N(1)–Co(1)–N(5)	178.2(2)	175.6(2) [178.7(3)]
N(1)–Co(1)–N(7)	95.6(2)	95.7(2) [94.8(3)]
N(1)–Co(1)–N(8)	86.3(2)	87.1(2) [86.3(3)]
N(2)–Co(1)–N(4)	85.6(2)	88.4(2) [86.3(4)]
N(2)–Co(1)–N(5)	95.77(19)	94.4(2) [95.6(3)]
N(2)–Co(1)–N(7)	177.1(2)	174.9(2) [175.7(3)]
N(2)–Co(1)–N(8)	94.7(2)	92.6(2) [93.5(3)]
N(4)–Co(1)–N(5)	82.91(19)	82.7(2) [82.4(3)]
N(4)–Co(1)–N(7)	97.0(2)	96.7(2) [97.8(4)]
N(4)–Co(1)–N(8)	177.9(2)	178.9(3) [176.4(3)]
N(5)–Co(1)–N(7)	85.9(2)	86.8(2) [86.5(3)]
N(5)–Co(1)–N(8)	94.97(19)	96.8(2) [94.1(3)]
N(7)–Co(1)–N(8)	82.7(2)	82.3(2) [82.5(3)]
N(3)–Co(2)–N(6)	113.70(19)	110.4(3) [110.6(3)]
N(3)–Co(2)–N(9)	110.5(2)	111.4(3) [110.3(3)]
N(6)–Co(2)–N(9)	108.9(2)	112.4(2) [114.8(2)]
N(3)–Co(2)–Cl(1)/Br(1)	106.49(15)	106.37(18) [109.5(2)]
N(6)–Co(2)–Cl(1)/Br(1)	106.29(15)	108.13(17) [108.06(17)]
N(9)–Co(2)–Cl(1)/Br(1)	110.91(16)	107.88(16) [103.31(18)]

mode and in turn three pyridine nitrogens are disposed to coordinate to the Co(2). The fourth coordination site of the Co(2) ion is satisfied by a chloride ion [2.226(2) Å] in **1** and a bromide ion [{2.3752(14) Å}/{2.3694(15)} Å] in **2**. In essence, in both the complexes three pyridine nitrogen and three deprotonated amide nitrogen atoms of L(−) provide the six coordination sites around a pseudo-octahedral Co(1) center. Significant deviation of the bond angles involving the chelation around Co(1) and Co(2) is observed (Table 1), presumably due to the formation of five-membered chelate rings with extended conjugation. The angles between *trans* atoms at the Co(1) center of $\mathrm{Co^{III}N(pyridine)_3N'(amide)_3}$ coordination spheres are in the range 177.1(2)–178.2(2)° for **1** and 174.9(2)° [175.7(3)°]–178.9(3)° [178.7(3)°] for **2**. The *cis* angles span a wide range 82.7(2)°–97.0(2)° for **1** and 82.3(2)° [82.4(3)°]–96.8(2)° [97.8(4)°] for **2**. The $\mathrm{Co^{II}N(pyridine)_3X}$ [X = Cl (**1**); X = Br (**2**)] coordination spheres are also severely distorted from ideal tetrahedral geometry. The angles span a wide range, 106.29(15)–113.70(19)° for **1** and 106.37(18)° [103.31(18)°]–112.4(2)° [114.8(2)°] for **2**. The marked distorted tetrahedral geometry around Co(2) in **1** and **2** is closely similar to that reported in the literature for a similar mixed-valence compound with grossly octahedral $\mathrm{Co^{III}}$ and distorted tetrahedral $\mathrm{Co^{II}}$ centers.[11b] Thus, intramolecular coexistence of both octahedral $\mathrm{Co^{III}N(pyridine)_3N'(amide)_3}$ ($S = 0$, see below) and tetrahedral $\mathrm{Co^{II}N(pyridine)_3(Cl/Br)}$ ($S = 3/2$, see below) coordination environment, supported by deprotonated pyridine amide ligand L(−), has been achieved.

The average $\mathrm{Co^{III}}$–N(py) and $\mathrm{Co^{III}}$–N(am) distances for six-coordinate Co(1) in **1** are 1.940(5) and 1.945(5) Å, for **2** 1.953(6) [1.953(8)] and 1.962(6) [1.944(7)] Å, respectively (Table 1). The average Co–N(py) distances for four-coordinate Co(2) in **1** and **2** are 2.018(5) Å and 2.033(6) [2.019(6)] Å, respectively (Table 1). In both the complexes **1** and **2** the Co–N(py) bond lengths around the Co(1) center are thus shorter than around Co(2). The observed differences in Co–N(py) bond lengths around two cobalt centers in both the complexes is quite obvious as in both the complexes Co(1) center is in the trivalent state and the Co(2) in the bivalent state. The $\mathrm{Co^{III}}$–N bond lengths are in good agreement with the reported values for pyridine amide complexes of trivalent cobalt.[2a,3e,6d,7e] The metric parameters of the metal centers in **1** and **2** are in good agreement with localized mixed-valence $\mathrm{Co^{III}Co^{II}}$ compounds in the solid state (Class I).[12] Complexes **1** and **2** provide a rare example of trapped-valence homonuclear bimetallic $\mathrm{Co^{III}Co^{II}}$ complexes.[11] To our knowledge, structure of the present group of complexes **1** and **2** are the first examples of mixed-valence transition metal dimers of a deprotonated pyridine amide ligand.

Crystal structure of $[\mathrm{Co^{III}Zn^{II}(L)_3(Cl)]Cl\cdot CH_3OH\cdot 5H_2O}$ (3).

A perspective view of the cation in $[\mathrm{Co^{III}Zn^{II}(L)_3(Cl)]Cl\cdot CH_3OH\cdot 5H_2O}$ (**3**) is displayed in Fig. 2 and selected bond distances and angles are collected in Table 2. The crystal structure analysis of the complex **3** reveals closely similar structural features as that observed in **1** and **2**. The fourth coordination site of the grossly tetrahedral $\mathrm{Zn^{II}}$ ion is satisfied by a chloride ion [2.2928(17) Å]. In essence, the three pyridine nitrogen and three deprotonated amide nitrogen atoms of L(−) ligand provide the six coordination sites around a pseudo-octahedral $\mathrm{Co^{III}}$ center. Significant deviation of the bond angles involving the chelation around $\mathrm{Co^{III}}$ and $\mathrm{Zn^{II}}$ is observed (Table 2). The angles between *trans* atoms at the $\mathrm{Co^{III}}$ center of $\mathrm{Co^{III}N(pyridine)_3N'(amide)_3}$ coordination spheres are in the range of 176.8(2)–178.1(2)°. The *cis* angles span a wide range 82.6(2)–96.4(2)° for **3**. The $\mathrm{Zn^{II}N(pyridine)_3Cl}$ coordination spheres are also severely distorted from ideal tetrahedral geometry in **3**. The angles span a wide range, 106.18(16)–111.18(17)° for **3**. The marked

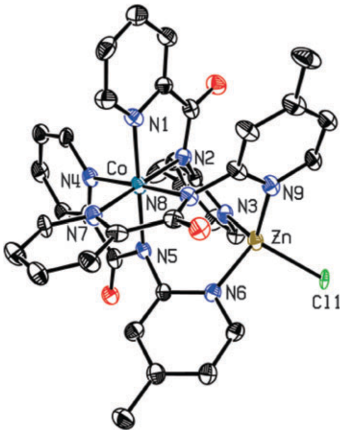


Fig. 2 View of $[Co^{III}Zn^{II}(L)_3(Cl)]^+$ in the structure of $[Co^{III}Zn^{II}(L)_3(Cl)]Cl{\cdot}CH_3OH{\cdot}5H_2O$ (**3**) with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°) in $[Co^{III}Zn^{II}(L)_3(Cl)]Cl{\cdot}CH_3OH{\cdot}5H_2O$ (**3**)

Co–N(1)	1.931(6)	Co–N(8)	1.968(5)
Co–N(2)	1.937(6)	Zn–N(3)	2.025(5)
Co–N(4)	1.948(5)	Zn–N(6)	2.020(6)
Co–N(5)	1.938(6)	Zn–N(9)	2.009(6)
Co–N(7)	1.931(6)	Zn–Cl(1)	2.2928(17)
N(1)–Co–N(2)	82.7(2)	N(4)–Co–N(8)	178.1(2)
N(1)–Co–N(4)	95.2(2)	N(5)–Co–N(7)	86.5(2)
N(1)–Co–N(5)	176.8(2)	N(5)–Co–N(8)	95.3(2)
N(1)–Co–N(7)	96.3(2)	N(7)–Co–N(8)	82.6(2)
N(1)–Co–N(8)	86.6(2)	N(3)–Zn–N(6)	111.0(2)
N(2)–Co–N(4)	86.3(2)	N(3)–Zn–N(9)	110.4(2)
N(2)–Co–N(5)	94.6(2)	N(6)–Zn–N(9)	111.1(2)
N(2)–Co–N(7)	177.2(2)	N(3)–Zn–Cl(1)	106.85(15)
N(2)–Co–N(8)	94.7(2)	N(6)–Zn–Cl(1)	106.18(16)
N(4)–Co–N(5)	83.0(2)	N(9)–Zn–Cl(1)	111.18(17)
N(4)–Co–N(7)	96.4(2)		

distorted tetrahedral geometry around Zn(II) in **3** is closely similar to that observed in complexes **1** and **2**.

The average Co^{III}–N(py) and Co^{III}–N(am) distances for six-coordinate Co^{III} in **3** are 1.936(6) and 1.947(6) Å, respectively (Table 2). The average Zn^{II}–N(py) distances in **3** is 2.018(6) Å (Table 2). The Co^{III}–N(py) bond lengths are shorter than the Zn^{II}–N(py) bond lengths, as expected. The Co^{III}–N bond lengths are in good agreement with the reported values for pyridine amide complexes of trivalent cobalt.[2a,3e,6d,7e]

To our knowledge, the structures of the present group of complexes **1–3** are the first examples of class I type mixed-valence homonuclear bimetallic and heteronuclear bimetallic complex, supported by a deprotonated pyridine amide ligand.

Non-covalent interactions

$[Co^{III,II}{}_2(L)_3(X)]X{\cdot}S$ [X = Cl (1); X = Br, S = CH_3OH (2)]. In **1**, intermolecular C–H···O contacts between amide O2 and C–H of 4-methylpyridine rings (pyridyl 6-H) are present (Table 3), leading to the formation of dimeric motifs *via* self-complementary hydrogen-bonding interactions (Fig. S3, ESI†).[18] Such dimeric units are involved in additional C–H···O contacts[13f,j,14,19–21] with neighbouring molecules *via* C–H (pyridyl 4-H of pyridine amide moiety) and amide O3 atom, affording a 1D chain (Fig. S4, ESI†). Furthermore, these 1D chains are involved in bifurcated C–H···Cl contacts[13a,b,e,g–k,19,20,22,23] with neighbouring molecules *via* C–H of pyridyl ring (pyridyl 6-H of 4-methyl-2-aminopyridine ring and pyridyl 4-H of pyridine amide moiety) and chloride anion, affording a 2D network (Fig. 3).

In **2**, intermolecular C–H···O contacts between amide O3 and C–H of the 4-methyl-2-aminopyridine ring (pyridyl 6-H) are present, leading to the formation of dimeric motifs *via* self-complementary hydrogen-bonding interactions (Fig. S5, ESI†),[18] as observed in the case of **1**. It has already been stated in the crystal structure description of complex **2** that the asymmetric unit of **2** contains two crystallographically independent molecules. In the crystal packing diagram it has been observed that one molecule interacts with other molecule *via* C–H···O hydrogen bonding interaction involving amide O1 and C–H of a 4-methyl-2-aminopyridine ring (pyridyl 6-H). The other C–H···O hydrogen bonding interaction involving amide O2′ and C–H of a 4-methyl-2-aminopyridine ring (pyridyl 3-H) is also present. Combination of these two interactions gives rise to a 2D network (Fig. S6, ESI†). These two molecules are also interconnected through C–H···Br hydrogen-bonding interaction. In fact, the C–H of a methyl group present on pyridine ring of one molecule, C–H (pyridyl 3-H) of another pyridine ring in the same molecule and C–H (pyridyl 4-H) of another molecule are involved in hydrogen-bonding interactions. The coordinated bromide is involved in C–H···Br hydrogen bonding with a methyl C–H of a 4-methyl-2-aminopyridine ring. From the same molecule, one pyridyl C–H is interacting with a non-coordinated bromide anion (Br2). This Br2 also interacts with the C–H (pyridyl 3-H) of a pyridine ring of another molecule giving rise to a 1D chain (Fig. S7, ESI†). When both C–H···O and C–H···Br interactions are considered together, this finally leads to the formation of a 3D network (Fig. S8 and S9, ESI†).

$[Co^{III}Zn^{II}(L)_3(Cl)]Cl{\cdot}CH_3OH{\cdot}5H_2O$ (3). As observed in the case of complexes **1** and **2**, in complex **3** also the intermolecular C–H···O contacts between amide O3 and C–H of 4-methylpyridine rings (pyridyl 6-H) are present, leading to the formation of dimeric motifs *via* self-complementary hydrogen-bonding interactions (Fig. S10, ESI†).[18] Such dimeric units are involved in C–H···Cl contacts[13a,b,e,g–k,19,20,22,23] with neighbouring molecules *via* C–H of a 4-methyl-2-aminopyridine ring (pyridyl 6-H) of other ligand and Zn^{II}-coordinated Cl(1), affording bimolecular 1D chains (Fig. S11, ESI†). Furthermore, these 1D chains are strengthened by additional C–H···O hydrogen-bonding involving C–H (pyridyl 4-H of a pyridine amide moiety) and amide O2. Actually, the Zn^{II}-coordinated Cl(1) ion is involved in a bifurcated C–H···Cl hydrogen-bonding interactions: (i) with the C–H of a 4-methyl-2-aminopyridine ring (pyridyl 6-H) of the neighbouring molecule in the same layer, which leads to the formation of 1D chain and (ii) with the C–H of a pyridine ring (pyridyl 4-H of a pyridine amide moiety) of the neighbouring molecule in the adjacent layer, which leads to the formation of a 2D network (Fig. 4).

The observed hydrogen-bonding parameters in this work C–H···O [2.30–2.34 Å and 134–151° (**1**); 2.31–2.56 Å and

Table 3 Hydrogen-bonding (C–H···O, C–H···Cl and C–H···Br) parameters for $[Co^{III,II}_2(L)_3(Cl)]Cl$ (**1**), $[Co^{III,II}_2(L)_3(Br)]Br{\cdot}CH_3OH$ (**2**) and $[Co^{III}Zn^{II}(L)_3\text{-}(Cl)]Cl{\cdot}CH_3OH{\cdot}5H_2O$ (**3**)

D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°	Sym. op. for A
$[Co^{III,II}_2(L)_3(Cl)]Cl$ (**1**)					
C12–H12···O2	0.95	2.34	3.071(9)	134[i]	[i] $2 - x, -y, -z$
C15–H15···O3	0.95	2.31[ii]	3.173(14)[ii]	151[iii]	[ii] $-1 + x, y, z$
					[iii] $1 + x, y, z$
C3–H3···Cl2B	0.95	2.87[iv]	3.441(10)[iv]	120	[iv] $1 - x, 1 - y, 1 - z$
C13–H13···Cl2B	0.95	2.62	3.399(9)	139	
$[Co^{III,II}_2(L)_3(Br)]Br{\cdot}CH_3OH$ (**2**)					
C11–H11···O2′	0.95	2.41[v]	3.231(8)[v]	145[v]	[v] $1 - x, 1 - y, -z$
C24–H24···O3	0.95	2.31[vi]	3.113(9)[vi]	142[vi]	[vi] $2 - x, -y, 1 - z$
C36–H36···O1	0.95	2.56[vii]	3.217(9)[vii]	127[vii]	[vii] $1 - x, -y, 1 - z$
C2–H2···Br2	0.95	2.97[viii]	3.775(10)[viii]	143[viii]	[viii] x, y, z
C10–H10C···Br1′	0.98	2.79[ix]	3.697(8)[ix]	154[x]	[ix] $x, 1 + y, z$
					[x] $x, -1 + y, z$
C27′–H27′···Br2	0.95	2.84[xi]	3.746(7)[xi]	161[xii]	[xi] $1 + x, y, 1 + z$
					[xii] $-1 + x, y, -1 + z$
$[Co^{III}Zn^{II}(L)_3(Cl)]Cl{\cdot}CH_3OH{\cdot}5H_2O$ (**3**)					
C12–H12···O3	0.95	2.41[xiii]	3.135(9)[xiii]	133[xiii]	[xiii] $1 - x, -y, -z$
C15–H15···O2	0.95	2.52[xiv]	3.340(14)[xiv]	144[xv]	[xiv] $-1 + x, y, z$
					[xv] $1 + x, y, z$
C24–H24···Cl1	0.95	3.06[xvi]	3.556(13)[xvi]	114[xvi]	[xvi] $-x, -y, -z$
C27–H27···Cl1	0.95	2.90[xvii]	3.627(15)[xvii]	134[xviii]	[xvii] $x, -1 + y, z$
					[xviii] $x, 1 + y, z$

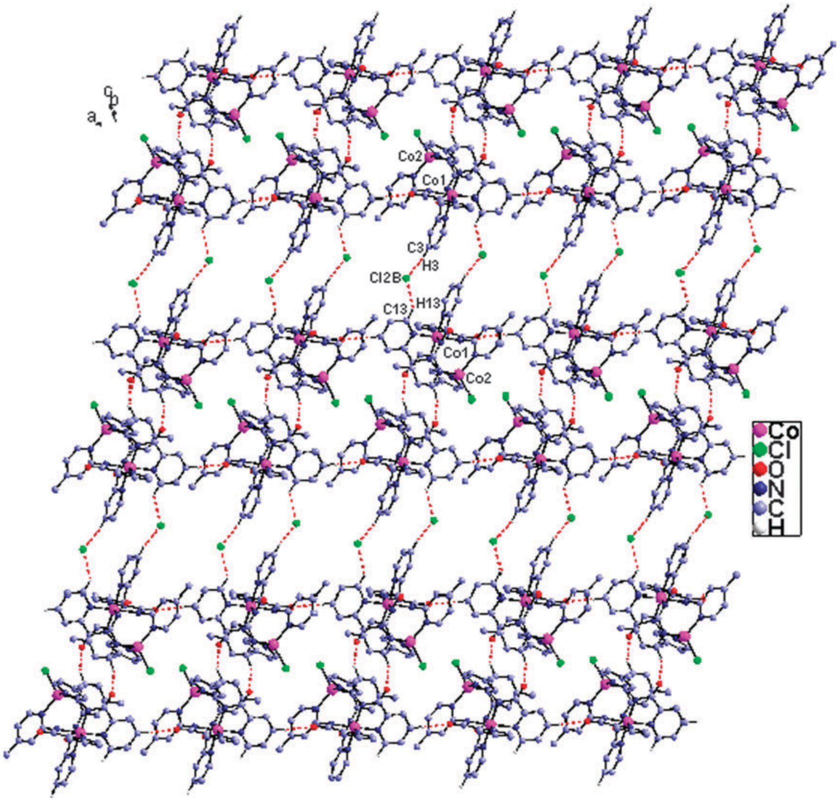


Fig. 3 View (*ab* plane) of the formation of a 2D network in $[Co^{III,II}_2(L)_3(Cl)]Cl$ (**1**) *via* C–H···Cl (interactions shown; involved atoms labelled) and C–H···O (interactions shown; involved atoms not labelled) hydrogen-bonding contacts. All the hydrogen atoms except those involved in hydrogen-bonding and a part of disordered chloride ion have been omitted for clarity. The 2D network is generated by the symmetry operators $2 - x, -y, -z$; $-1 + x, y, z$; $1 + x, y, z$ and $1 - x, 1 - y, 1 - z$.

127–145° (**2**); 2.41–2.52 Å and 133–144° (**3**)], C–H···Cl [2.62–2.87 Å and 120–139° (**1**); 2.90–3.06 Å and 114–134° (**3**)] and C–H···Br [2.79–2.97 Å and 143–161° (**2**)] are in good agreement with literature tabulations (C–H···Cl: 2.569–2.944 Å and 119.3–169.2°; C–H···O: 2.045–2.399 Å and 90.7–176.7°; C–H···Br: 2.66–3.09 Å and 113–171°),[20,24a] literature

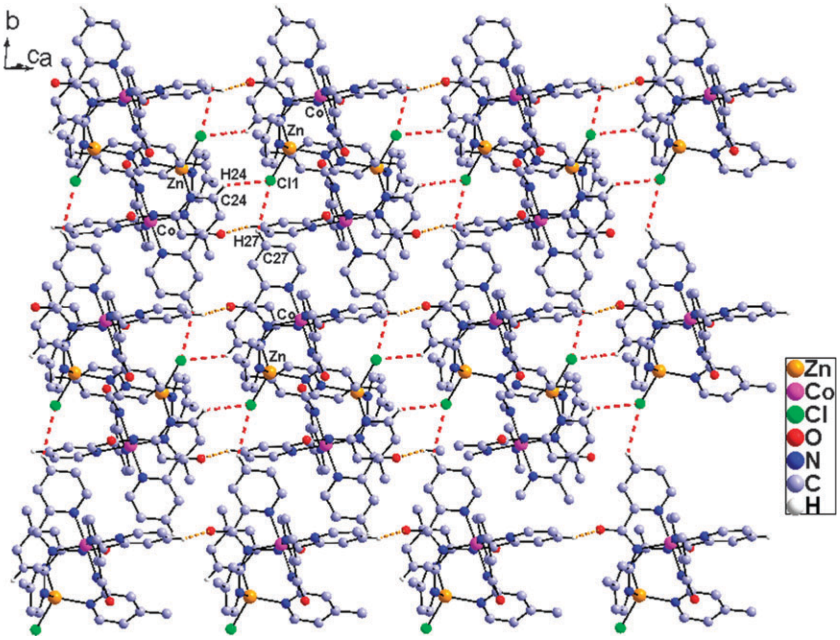


Fig. 4 View (*bc* plane) of the formation of 2D network in [$Co^{III}Zn^{II}(L)_3(Cl)$]Cl·CH_3OH·5H_2O (**3**) *via* C–H···Cl and C–H···O hydrogen-bonding contacts. All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity. The 2D network is generated by the symmetry operators $x, -1 + y, z$; $x, 1 + y, z$; $-x, -y, -z$; $-1 + x, y, z$ and $1 + x, y, z$.

precedents[14a,19,21–23,24b] including our own findings.[13] The C–H···O hydrogen-bonding interactions could be considered as strong,[19b] C–H···Cl interactions as moderate[19b] and weak[19c] and C–H···Br interactions as moderate in strength.[19b]

Magnetism

As a representative of two homonuclear bimetallic mixed-valence $Co^{III}Co^{II}$ complexes **1** and **2**, solid-state magnetic susceptibility measurements were performed for a very fresh sample of **1** in the range of 2–300 K. On the basis of the structure of **1**, the only unpaired electrons will be on the Co^{II} center, as the Co^{III} ions are low-spin ($t_{2g}{}^6$, $S = 0$). The $\chi_M T$ product (χ_M = molar magnetic susceptibility) decreases gradually from the room-temperature value of 2.25 cm^3 mol^{-1} K at 300 K. The room-temperature value is larger than the spin-only value $S = 3/2$ ion (1.875 cm^3 mol^{-1} K). Tetrahedral Co^{II} has an orbital singlet $^4A_2$ ground state which, in the presence of axial distortions, is split into two Kramers doublets: $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$.[11c] Such a zero field splitting is the most important source of paramagnetic anisotropy. An appropriate Hamiltonian[11c] was used to fit the temperature-dependent magnetic susceptibility data for **1**, in which the only paramagnetic center is the pseudo-tetrahedral Co^{II} ion. The data with its best-fit are shown in Fig. S12 (ESI†). In this case, its magnetic behaviour is corresponding to a spin-only $S = 3/2$ with a zero-field splitting parameter (2*D* is the energy gap between the two Kramers doublets $M_s = |\pm 3/2\rangle$ and $|\pm 1/2\rangle$). The best-fit *g* and *D* values are 2.20 and 3.9 cm^{-1}, respectively. These values are in the ranges 2.2–2.4 for *g* and 1 to ~15 cm^{-1} for *D* observed for single Co^{II} ions in distorted tetrahedral environments.[11c] The solution state (Evans' method[25a]) value at 300 K of 4.24 μ_B is in good agreement with that obtained in the solid state. The values are near to that expected for a Co^{II} ion ($S = 3/2$) leaving little doubt that one of the cobalt ions is in the trivalent state and observed values are comparable to that reported for similar trapped mixed-valence compounds.[11b,c]

Redox properties

The redox behaviour of complexes **1–3** has been studied by cyclic voltammetry (CV). The CV scan of each complex in CH_3CN at a platinum working electrode revealed a one-electron $Co^{III}Co^{II}/Co^{II}Co^{II}$ reductive response at $E_{1/2}$ (ΔE_p) values [V *vs.* SCE (mV)] of −0.31 (80), −0.29 (100) and −0.30 (160), respectively. The CV scan of **1** is displayed in Fig. S13 (ESI†). When the complexes **1** and **2** were scanned anodically in the range 0.0–2.0 V no well-defined oxidative response was observed due to the $Co^{III}Co^{III}/Co^{III}Co^{II}$ redox process.

Conclusion

In this work utilizing a pyridine amide ligand with potentially three donor sites we have synthesized and structurally characterized two homobinuclear mixed-valence $Co^{III}Co^{II}$ complexes and a heterobinuclear $Co^{III}Zn^{II}$ complex. Structural studies reveal that the Co^{III} centre is in distorted octahedral and the Co^{II} or Zn^{II} centre is in distorted tetrahedral geometry. An analysis of the crystal packing diagram of these compounds reveals the existence of interesting non-covalent interactions (C–H···O, C–H···Cl and C–H···Br), leading to the formation of 1D, 2D and 3D supramolecular architectures. Solid and solution-state magnetic susceptibility measurements on a representative mixed-valence $Co^{III}Co^{II}$ complex confirm that the trivalent cobalt is in low-spin state and the bivalent cobalt is in high-spin state. Complexes **1** and **2** are examples of Class-I mixed-valence compounds.

Experimental

General remarks

All reagents were obtained from commercial sources and used as received. Solvents were dried/purified as reported previously.[2,6] Tetra-*n*-butylammonium perchlorate (TBAP) was prepared by following a reported procedure.[2,6] The methodology followed to prepare the ligand HL is adapted from Barnes *et al.*[13b]

Syntheses

4-Methyl-2-(*N*-(2-pyridyl)carbamoyl)pyridine (HL). To a stirred solution of pyridine-2-carboxylic acid (2 g, 16.3 mmol) in 10 cm^3 of pyridine was added 2-amino-4-methylpyridine (1.76 g, 16.3 mmol) in 5 cm^3 of pyridine, dropwise. Triphenylphosphite (5.05 g, 16.3 mmol) was added to the reaction mixture dropwise. The reaction mixture was heated at 100 °C with stirring for 5 h. The volume of the reaction mixture was then reduced to about half of its original volume and was washed three times with distilled water. The resulting light brown oil was taken in 50 cm^3 of CH_2Cl_2 and was extracted into 100 cm^3 of aqueous HCl (1 : 1, v/v). The acidic aqueous extract was neutralized by solid sodium bicarbonate. The resulting off-white product was filtered off, washed thoroughly with distilled water, and recrystallized from CH_3OH as needles (yield: 2.84 g, *ca.* 82%). Anal. Calc. for $C_{12}H_{11}N_3O$: C, 67.62; H, 5.16; N, 19.72. Found: C, 68.12; H, 5.28; N, 18.84%. IR data: ν_{NH} 3344 cm^{-1} and ν_{CO} 1695 cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.8 (br, 1H), 8.85 (d, 1H), 8.35 (t, 2H), 8.05 (d, 1H), 7.85 (d, 1H), 7.4 (d, 1H), 7.2 (d, 1H), 2.5 (s, 3H).

[$Co^{III,II}_2(L)_3(Cl)$]Cl (1). To a stirred solution of HL (0.051 g, 0.24 mmol) in CH_3CN (4 cm^3) was added solid $CoCl_2\cdot 4H_2O$ (0.038 g, 0.16 mmol) and K_2CO_3 (0.011 g, 0.08 mmol). A bluish solution with white turbidity was obtained, which was filtered and collected the clean blue solution. After reducing the volume, diethyl ether was added as precipitant. The blue product obtained was filtered off, washed with Et_2O and air-dried. Yield: 64%, based on composition [$Co^{III,II}_2(L)_3(Cl)$]Cl. X-Ray quality crystals of composition [$Co^{III,II}_2(L)_3(Cl)$]Cl were obtained by vapour diffusion of ethyl acetate to a CH_3CN solution of the complex. Anal. Calc. for $C_{36}H_{31}Cl_2Co_2N_9O_{3.5}$: C, 51.9; H, 3.7; N, 15.1. Found: C, 51.3; H, 3.6; N, 15.1%. IR (KBr, cm^{-1}, selected peaks): 3450 ν(OH) and 1625 ν(C=O). Molar conductance, Λ_M (CH_3CN, $\sim 10^{-3}$ M, 298 K) = 150 Ω^{-1} cm^2 mol^{-1}. UV/Vis (CH_3CN) [λ_{max}/nm (ε/M^{-1} cm^{-1})] 255 sh (22 120), 325 sh (10 650), 555 (575), 580 (550), 1040 (20).

[$Co_2^{III,II}(L)_3(Br)$]Br·CH_3OH (2). The complex **2** was synthesized following the method adopted for the synthesis of complex **1** using $CoBr_2\cdot 4H_2O$ as the source of metal salt. Yield: 62%, based on composition [$Co_2^{III,II}(L)_3(Br)$]Br. Single-crystals suitable of composition [$Co_2^{III,II}(L)_3(Br)$]Br·CH_3OH for X-ray diffraction were obtained by vapour diffusion of Et_2O to a CH_3OH solution of the complex. Anal. Calc. for $C_{37}H_{34}Br_2Co_2N_9O_4$: C, 46.8; H, 3.6; N, 13.3. Found: C, 46.9; H, 3.6; N, 13.1%. IR (KBr, cm^{-1}, selected peaks): 3436 ν(OH) and 1637 ν(C=O). UV/Vis (in CH_3CN) [λ_{max}/nm (ε/M^{-1} cm^{-1})] 255 sh (42 510), 325 sh (16 170), 560 (930), 590 (800), 615 sh (550), 1080 (24).

[$Co^{III}Zn^{II}(L)_3(Cl)$]Cl·CH_3OH·$5H_2O$ (3). To a stirred solution of HL (0.050 g, 0.23 mmol) in CH_3CN (5 cm^3) was added K_2CO_3 (0.011 g, 0.08 mmol) and then solid $CoCl_2\cdot 4H_2O$ (0.019 g, 0.08 mmol). After 0.5 h, $ZnCl_2$ (0.011 g, 0.08 mmol) was added to it. After stirring for 4 h the reaction mixture was filtered and collected the clean pink solution. After reducing the volume to half of its original volume, Et_2O was added as precipitant. The compound that precipitated was filtered off, washed with Et_2O and air-dried. Yield: 60%. Single crystals suitable for X-ray diffraction were obtained by layering of Et_2O to a solution of the complex in a mixture of CH_3CN and CH_3OH. Anal. Calc. for $C_{36}H_{42}Cl_2CoN_9O_9Zn$: C, 46.0; H, 4.5; N, 13.4. Found: C, 46.1; H, 4.4; N, 13.5%. IR (KBr, cm^{-1}, selected peaks): 3451 ν(OH) and 1641 ν(C=O). ^1H NMR (CD_3CN, 500 MHz): δ (ppm) 8.48 (d, J = 5.5 Hz, 3H; H_6 of py), 8.28 (t, J = 8.2 Hz, 3H; H_4 of py), 7.86 (d, J = 7.5 Hz, 3H; $H_{6'}$ of py), 7.80 (m, 6H; $H_{3,5}$ of py), 7.25 (d, J = 5.5 Hz, 3H; $H_{3'}$ of py), 6.84 (d, J = 7.4 Hz, 3H; $H_{5'}$ of py), 1.83 (s, 9H; CH_3). UV/Vis (in CH_3CN) [λ_{max}/nm (ε/M^{-1} cm^{-1})] 255 sh (22 200), 280 sh (20 160), 330 (11 620), 540 (480).

Physical measurements

Elemental analyses were obtained using Thermo Quest EA1110 CHNS-O, Italy. Conductivity measurements were done with an Elico type CM–82T conductivity bridge (Hyderabad, India). Spectroscopic measurements were made using the following instruments: IR (KBr, 4000–600 cm^{-1}), Bruker Vector22; electronic, Perkin Elmer Lambda 2 and Agilent 8453 diode array spectrophotometer. ^1H NMR spectral measurements were performed on a JEOL-LA-500 FT (500 MHz) NMR spectrometer. Magnetic susceptibility measurements on polycrystalline sample of **1** were performed with a Quantum Design SQUID magnetometer (València, Spain). Solution-state magnetic susceptibilities were obtained by the NMR technique of Evans[25a] in MeCN with a PMX-60 JEOL (60 MHz) NMR spectrometer. Corrections underlying diamagnetism were applied with the use of appropriate constants.[25b] The cyclic voltammetric experiments were performed at 298 K by using a CH Instruments, Electrochemical Analyzer/Workstation Model 600B Series. A standard three-electrode cell was employed with a Beckman M-39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode and a saturated calomel electrode (SCE) as reference; no corrections were made for junction potentials. Details of cell configuration and criterion for reversibility are as reported previously.[2,6]

Single-crystal X-ray structure determination

Single crystals of suitable dimension of complexes **1–3** were used for data collection. Diffracted intensities were collected on a Bruker SMART APEX CCD diffractometer, with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation at 100(2) K. For data reduction the 'Bruker Saint Plus' program was used. Empirical absorption correction (SADABS) was applied to data sets. Structures were solved by the direct method using SHELXS-97 and refined on F^2 by a

Table 4 Crystal data and structure refinement for $[Co^{III,II}_2(L)_3(Cl)]Cl$ (**1**), $[Co^{III,II}_2(L)_3(Br)]Br\cdot CH_3OH$ (**2**) and $[Co^{III}Zn^{II}(L)_3(Cl)]Cl\cdot CH_3OH\cdot 5H_2O$ (**3**)

	1	**2**	**3**
Formula	$C_{36}H_{30}Cl_2Co_2N_9O_3$	$C_{37}H_{34}Br_2Co_2N_9O_4$	$C_{37}H_{44}Cl_2CoN_9O_9Zn$
M_r	825.45	946.41	954.01
Crystal colour, habit	Blue, block	Blue, block	Pink, block
T/K	100(2)	100(2)	100(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	11.573(5)	12.340(5)	11.555(5)
b/Å	11.596(5)	16.429(5)	12.482(5)
c/Å	16.367(5)	20.045(5)	16.117(5)
α/°	76.960(5)	93.162(5)	78.089(5)
β/°	81.580(5)	94.169(5)	72.040(5)
γ/°	66.012(5)	93.594(5)	86.649(5)
U/Å^3	1951.3(13)	4038(2)	2163.6(14)
Z	2	4	2
D_c/g cm^{-3}	1.405	1.557	1.123
μ/mm^{-1}	1.033	2.850	1.46
Reflections measured	13 140	26 746	10 253
Unique reflections (R_{int})	9315 (0.0359)	19 176 (0.0407)	10 253 (0.0000)
Reflections used [$I > 2\sigma(I)$]	6235	10 026	4663
$R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0820, 0.1973	0.0885, 0.2206	0.0872, 0.2244
$R_1{}^a$, $wR_2{}^b$ (all data)	0.1215, 0.2465	0.1497, 0.2832	0.1527, 0.2691
GOF on F^2	1.120	1.230	0.887

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[w(|F_o|^2)^2]\}^{1/2}$.

full-matrix least-squares technique using the SHELXL-97[26a] program package. For all three structures the position of the hydrogen atoms associated with carbon atoms of the ligand were calculated assuming ideal geometries. The hydrogen atoms at C34 for **1** and C34 and C34′ for **2** were located from difference Fourier map and not refined. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedure on F^2. The chloride counteranion in **1** was displaced over two positions and they were refined with a site occupation factor of 0.5/0.5. The data set of **3** was treated with the SQUEEZE filter of PLATON[26b] due to the presence of severely disordered solvent molecules and counter anion which could not be modeled satisfactorily. The SQUEEZE process reported that the disordered solvent and chloride components accounted for 171 electrons per unit cell or half that number that is 85.5 (one methanol, five water and one chloride) per cation in a volume of 571.0 Å^3 out of a unit volume of 2163.6 Å^3. These disordered molecules were included in the final chemical formula (Table 4). The values of $F(000)$, D_c, M (molecular formula weight) and μ have been calculated on this assumption. Pertinent crystallographic parameters are summarized in Table 4. After anisotropic refinement for **1**, **2** and **3** some unassigned electron density peaks (**1**: a peak of 1.68 e Å^{-3} was found near Cl2A at a distance of 2.26 Å; **2**: a peak of 2.58 eÅ^{-3} was found near Co1 at a distance of 0.07 Å; **3**: a peak of 1.76 e Å^{-3} was found near Cl1 at a distance of 0.23 Å) were observed in the final difference Fourier map, which must be due to the poor quality of crystal chosen for data collection. For complex **2** some of the carbon atoms of some rings showed large displacement parameters. This may be due to the poor quality of crystals chosen for data collection and poor dataset obtained. Unfortunately, we could not grow single crystals of **1–3** (particularly for **3**) that were any better than the one used for the present study, as they were the best we could have. It should be noted here that in complex **1** the chloride counter anion is displaced over two positions. For clarity only one part of disordered chloride counter anion (see above) is shown in secondary interactions. Intermolecular contacts of the C–H···O, C–H···Cl and C–H···Br type were examined with the DIAMOND package.[26c]

Acknowledgements

This work is supported by grants from the Council of Scientific and Industrial Research and Department of Science and Technology, Government of India, New Delhi. W. J. and H. M. gratefully acknowledge the award of fellowships (SRF) by CSIR and UGC, respectively.

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