

Methylene Spacer-Regulated Structural Variation in Cobalt(II/III) Complexes with Bridging Acetate and Salen- or Salpn-Type Schiff-Base Ligands

Shouvik Chattopadhyay,^[a,bl] Michael G. B. Drew,^[cl] and Ashutosh Ghosh^{*[al]}

Keywords: Cobalt / Mixed valence / Schiff base / N₂O₂ ligands / Crystal structures / DFT calculations

Two linear, trinuclear mixed-valence complexes, [Co^{II}{(μ-L¹)-(μ-OAc)Co^{III}(OAc)}₂] (**1**) and [Co^{II}{(μ-L²)-(μ-OAc)Co^{III}(OAc)}₂] (**2**) and two mononuclear Co^{III} complexes [Co^{III}{L³}(OAc)] (**3**), and [Co^{III}{L⁴}(OAc)] (**4**) were prepared and the molecular structures of **1**, **2** and **4** elucidated on the basis of X-ray crystallography [OAc = Acetate ion, H₂L¹ = H₂Salen = 1,6-bis(2-hydroxyphenyl)-2,5-diazahepta-1,5-diene, H₂L² = H₂Me₂Salen = 2,7-bis(2-hydroxyphenyl)-2,6-diazaocta-2,6-diene, H₂L³ = H₂Salpn = 1,7-bis(2-hydroxyphenyl)-2,6-diazahepta-1,6-diene, H₂L⁴ = H₂Me₂Salpn = 2,8-bis(2-hydroxyphenyl)-3,7-diazanona-2,7-diene]. In complexes **1** and **2**, the acetate groups show both monodentate and bridging bidentate coordination modes, whereas chelating bidentate acetate is present in **4**. The terminal Co^{III}N₂O₄ centres in **1** and **2** exhibit

uniform facial arrangements of both non-bridged N₂O and bridging O₃ donor sets and the Co^{II} centre is coordinated to six (four phenoxo and two acetato) oxygen atoms of the bridging ligands. The effective magnetic moment at room temperature corresponds to the presence of high-spin Co^{II} in both **1** and **2**. The complexes **1** and **2** are thus Co^{III}(S = 0)–Co^{II}(S = 3/2)–Co^{III}(S = 0) trimers. Complexes **3** and **4** are monomeric and diamagnetic containing low-spin Co^{III}(S = 0) with chelating tetradentate Schiff base and bidentate acetate. Calculations based on DFT rationalise the formation of trinuclear or mononuclear complexes.

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Introduction

Cobalt-Salen related systems have a wide range of applications: they are used as catalysts for the oxygenation of organic molecules, they can act as antiviral agents, due to their ability to interact with proteins and nucleic acids, and they have been used to mimic biological co-factors, such as cobalamin.^[1–7] Salen-type ligands are also significant because of the fascinating ability of the phenoxo oxygen atoms to form μ²-bridges thus affording high-nuclearity complexes which could act as promising candidates to offer valuable insights into various natural electron-transfer events.^[8] High-nuclearity coordination complexes achieved by these types of ligand along with other appropriate co-ligands provide tractable examples to rationalise magnetic exchange phenomenon^[9,10] emerging from temperature-dependent interaction between the spin states of individual magnetic centres. Amongst multinuclear complexes of transition metals, cyclic trinuclear cobalt complexes form an important class^[11] as they have been found to show some catalytic activity in the epoxidation of olefins^[12] and in the

auto-oxidation of hydrocarbons.^[13] Linear trinuclear Co^{III}–(S = 0)–Co^{II}(S = 3/2)–Co^{III}(S = 0) complexes containing deprotonated Schiff base are rare and to the best of our knowledge only three such structures have been reported so far.^[14] One is [Co^{II}Co^{III}₂(SO₃)₂(Me₂Salpn)₂(*n*PrOH)₂]·*n*PrOH^[14a] which was obtained by the reduction of corresponding Co^{III} complexes by SO₂. The other two complexes are [Co^{II}{(μ-Salen)(μ-OAc)Co^{III}(NCS)}₂]^[14b] and [Co^{II}(μ-Salpn)₂(μ-OAc)₂Co^{III}(NCS)₂]^[14c] both of which have been prepared by oxidation of the Co^{II} salt [H₂Salen = 1,6-bis(2-hydroxyphenyl)-2,5-diazahepta-1,5-diene, H₂Salpn = 1,7-bis(2-hydroxyphenyl)-2,6-diazahepta-1,6-diene, H₂Me₂Salpn = 2,8-bis(2-hydroxyphenyl)-3,7-diazanona-2,7-diene].

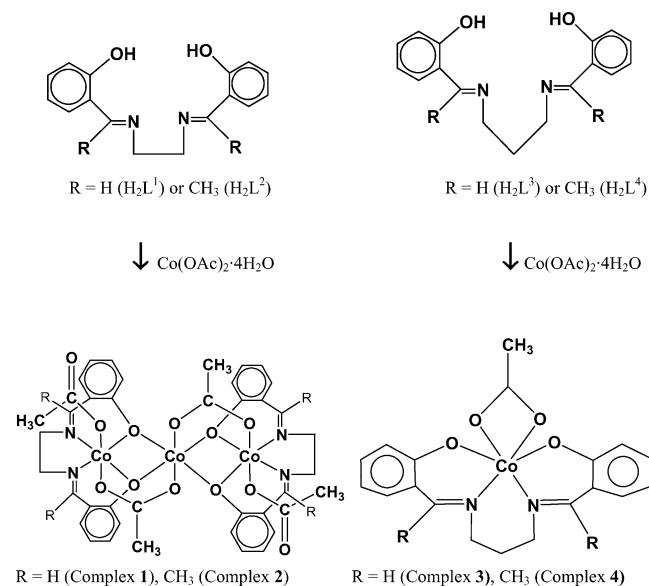
Our attempts with Salen (H₂L¹) and H₂Me₂Salen, i.e. 7-bis(2-hydroxyphenyl)-2,6-diazaocta-2,6-diene (H₂L²), as representatives of the quadridentate bis(salicylidene)-type Schiff-base ligands family, furnished novel Co^{III}–Co^{II}–Co^{III} mixed-valence linear trinuclear species, whereas the ligands, Salpn (H₂L³) and Me₂Salpn (H₂L⁴) afforded mononuclear Co^{III} complexes (Scheme 1). X-ray crystal structure determinations of three of these complexes have established their structures. Thus, the use of bis(salicylidene) ligands with polymethylene spacers of varying flexibility allowed us to regulate their electronic and steric demands which could effectively modulate structural versatility enlightening spin and valence change phenomena.

Herein, we report the synthesis, spectroscopic characterisations and room-temperature magnetic moments of four

[a] Department of Chemistry, University College of Science, University of Calcutta, 92 A.P.C. Road, Kolkata 700009, India
E-mail: ghosh_59@yahoo.com

[b] Department of Chemistry, Jhargram Raj College, Jhargram, West Midnapore 721507, West Bengal, India

[c] School of Chemistry, The University of Reading, P. O. Box 224, Whiteknights, Reading RG6 6AD, UK



Scheme 1.

complexes. Three of them have been characterised by X-ray crystallography. Density Functional Theory with the B3LYP methodology is used to rationalise the formation of trimeric or monomeric complexes with the incorporation of a CH_2 spacer in the diamine chain.

Results and Discussion

Syntheses

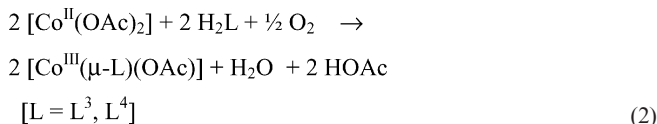
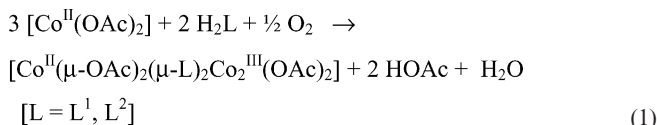
Facile condensation of 1,2-diaminoethane or 1,3-diaminopropane in 1:2 molar ratio with salicylaldehyde and 2-hydroxyacetophenone separately, afforded four neutral condensates, H_2Salen , H_2Salpn , $\text{H}_2\text{Me}_2\text{Salen}$ and $\text{H}_2\text{Me}_2\text{Salpn}$ (general abbreviations H_2L^1 , H_2L^2 , H_2L^3 and H_2L^4 , respectively, where H atoms are dissociable phenolic hydrogens), which have been employed as the tetradentate chelating ligands in the present work (Scheme 1).

Methanol solution of $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$ was added separately in a methanol solution of H_2L^1 and H_2L^2 in 3:2 molar ratio with constant stirring at ambient temperature. It was kept for 2 days to separate brown compounds. Subsequent crystallisation of the product from dichloromethane solution gave brown crystals of the trinuclear mixed-valence cobalt complexes (**1** and **2**) as authenticated by X-ray structure determinations (Scheme 1).

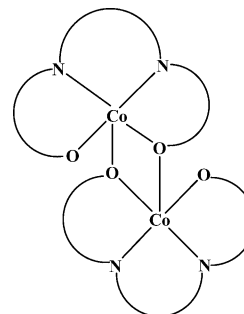
However, when we added methanol solution of $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$ to the ligands H_2L^3 and H_2L^4 in the same molar ratio (3:2), monomeric compounds **3** and **4** were formed (instead of the formation of trimeric analogues of **1** and **2**), both of which contained Co^{III} with chelating acetate (Scheme 1) as was evident from the X-ray structure determination of **4**. We failed to grow the single crystal of complex **3** and it was characterised by IR and UV/Vis spectra, elemental analysis, mass spectra and magnetic moment measurement. To obtain the trinuclear compounds with li-

gands H_2L^3 and H_2L^4 we increased the metal/ligand ratio (up to 2:1) but we always obtained as product the mononuclear complexes **3** and **4**. On the other hand, for the ligands H_2L^1 and H_2L^2 even if we decreased the metal/ligand ratio to 1:1, we did not obtain any mononuclear Co^{III} complexes analogous to **3** and **4**, instead trinuclear complexes (**1** and **2**) resulted invariably. Thus, irrespective of the molar ratio of metal and ligand, H_2Salen and $\text{H}_2\text{Me}_2\text{Salen}$ formed trinuclear complexes whereas H_2Salpn and $\text{H}_2\text{Me}_2\text{Salpn}$ yielded mononuclear complexes.

To investigate the importance of air oxidation, the reactions were performed under N_2 atmosphere leading to a red compound being obtained as the product, which was identified as a mononuclear Co^{II} complex ($[\text{CoL}]$, $\text{L} = \text{L}^1, \text{L}^2, \text{L}^3, \text{L}^4$) by IR spectra, elemental analysis and mass spectra. The formation of no complex with Co^{III} logically tempted us to believe that atmospheric oxygen here acted as an external oxidant according to the Equations (1) and (2).



Again, **1**, **2**, **3** and **4** could be reduced by N_2H_4 to a reddish brown gelatinous precipitate. These were monomeric cobalt(II) complexes. Amongst these, diffraction quality dark red-brown single crystals of a cobalt(II)-Salen complex were collected by maintaining the reaction flask at about 40°C for two days under N_2 atmosphere. The dimeric structure (Scheme 2) of this compound has been reported elsewhere by another group.^[15]

Scheme 2. A sketch of the dimeric $\text{Co}(\text{Salen})$ compounds.

Structure Description: **1** and **2**

The trinuclear structures of **1** and **2** as shown in Figures 1 and 2, each contain three cobalt atoms in an approxi-

mately linear arrangement. The data for **2** are poor because the crystal gave a very weak diffraction pattern but it is clear that the dimensions are very similar to those found in **1**. Each cobalt atom has a six-coordinate octahedral environment. In both structures the central cobalt atom Co(1) is bonded to four oxygen atoms forming an equatorial plane, O(31) and O(50) from one ligand and O(11) and

O(30) from another. These oxygen atoms are also bridging to one of the two outer cobalt atoms Co(2) and Co(3). Molecular dimensions are given in Tables 1 and 2 and confirm that Co(1) has oxidation state (II) and Co(2) and Co(3) oxidation state (III). This is indicated by the fact that these oxygen atoms are bound more strongly to the Co(2) and Co(3) with distances ranging from 1.840(5)–1.924(4) Å in

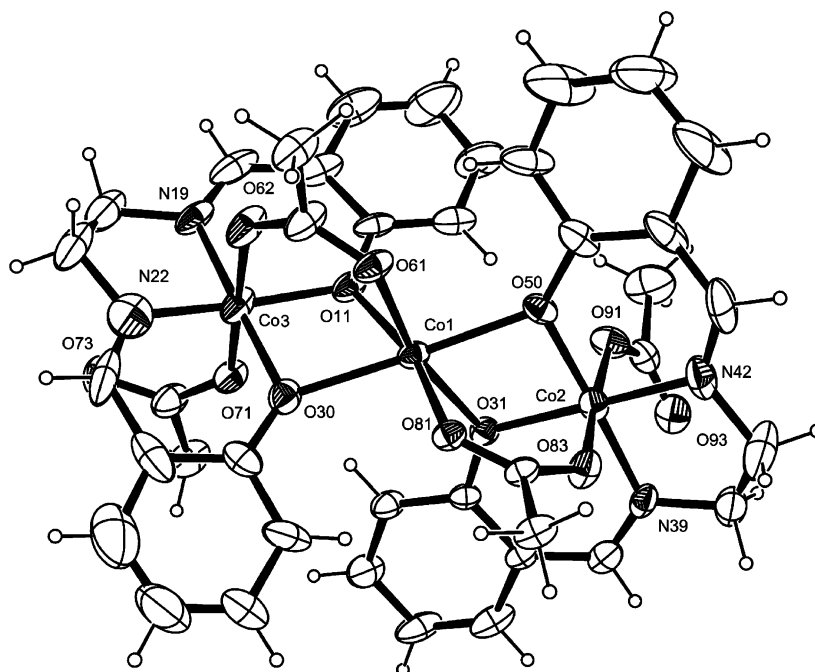


Figure 1. The structure of **1** with ellipsoids at 25% probability.

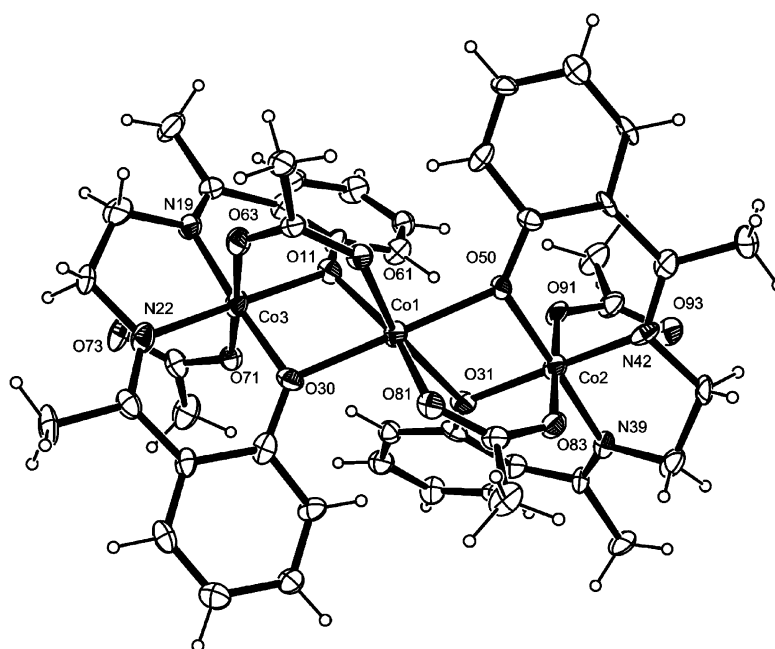


Figure 2. The structure of **2** with ellipsoids at 25% probability.

the two structures compared to Co(1)–O distances of 2.070(6)–2.173(5) Å. To complete the metal coordination sphere of Co(1), there are two bridging acetates with oxygen atoms O(61) and O(81) in mutually *cis* positions at distances ranging from 2.023(6)–2.082(6) Å. These acetates form bridges to the adjacent cobalt atoms such that Co(3) is bonded to O(63) at 1.924(4), 1.923(6) Å in the two structures and Co(2) is bonded to O(83) at 1.908(3), 1.900(6) Å in the two structures. The coordination spheres of Co(2) and Co(3) are completed with two nitrogen atoms of the ligand [1.810(9)–1.902(8) Å] and an oxygen atom from a monodentate acetate with distances Co(2)–O(91) 1.901(4), 1.884(6) Å and Co(3)–O(71) 1.898(4), 1.846(7) Å in **1** and **2**, respectively.

Table 1. Selected bond lengths for compounds **1** and **2**.

	1	2
Co(1)–O(61)	2.037(3)	2.082(6)
Co(1)–O(81)	2.038(3)	2.023(6)
Co(1)–O(11)	2.112(3)	2.151(7)
Co(1)–O(31)	2.123(3)	2.173(5)
Co(1)–O(50)	2.137(3)	2.086(6)
Co(1)–O(30)	2.143(3)	2.070(6)
Co(2)–N (42)	1.858(5)	1.825(8)
Co(2)–O(50)	1.888(4)	1.887(5)
Co(2)–N (39)	1.888(5)	1.871(7)
Co(2)–O(91)	1.901(4)	1.884(6)
Co(2)–O(83)	1.908(3)	1.900(6)
Co(2)–O(31)	1.911(3)	1.882(6)
Co(3)–N (22)	1.810(9)	1.902(8)
Co(3)–N (19)	1.865(6)	1.840(8)
Co(3)–O(30)	1.895(4)	1.840(6)
Co(3)–O(71)	1.898(4)	1.846(7)
Co(3)–O(11)	1.914(4)	1.904(5)

The intramolecular separations between Co(2)⋯Co(1) are 3.074 and 3.059 Å in **1** and **2** respectively, whereas Co(1)⋯Co(3) separations are 3.075 in **1** and 3.051 Å in **2**. None of these distances are sufficiently short to imply any metal–metal bonding or allow intra-metal spin exchange through mutual interaction. The bridging angles, Co(1)–O(50)–Co(2), Co(1)–O(31)–Co(2), Co(1)–O(30)–Co(3) and Co(1)–O(11)–Co(3), 99.5(2), 99.1(1), 99.0(2) and 99.5(2) in complex **1** and 100.6(3), 97.7(3), 102.4(3) and 97.4(2) in complex **2**, indicate non-collinear Co^{III}–O–Co^{II} fragments, not suitable for significant electronic exchange.

In complex **1**, O(73) of one of the terminal acetate moieties is involved in hydrogen bonding with H(101) of a water molecule present in the crystal (Table 3). The other hydrogen of the same water molecule, H(102), forms an H-bond with a symmetry related (1 –y, x, 2 –z) oxygen atom, O(93') of a terminal acetate ligand. Similarly, H(102'), H(102'') and H(102''') are hydrogen bonded with O(93''), O(93''') and O(93) ('' = y, 1 –x, 2 –z, ''' = 1 –x, 1 –y, z) respectively to form a cyclic dodecanuclear tetramer of complex **1** (Figure 3). There is no such H-bond present in complex **2**.

Table 2. Selected bond angles for compounds **1** and **2**.

	1	2
O(61)–Co(1)–O(81)	88.46(13)	89.0(2)
O(61)–Co(1)–O(11)	87.84(14)	84.8(2)
O(81)–Co(1)–O(11)	165.52(15)	163.2(2)
O(61)–Co(1)–O(31)	164.56(14)	162.1(2)
O(81)–Co(1)–O(31)	87.29(12)	83.2(2)
O(11)–Co(1)–O(31)	99.74(13)	106.9(2)
O(61)–Co(1)–O(50)	92.63(15)	90.8(2)
O(81)–Co(1)–O(50)	86.64(13)	87.9(2)
O(11)–Co(1)–O(50)	107.51(15)	107.8(2)
O(31)–Co(1)–O(50)	72.31(12)	72.9(2)
O(61)–Co(1)–O(30)	84.22(15)	88.9(2)
O(81)–Co(1)–O(30)	92.93(14)	92.6(2)
O(11)–Co(1)–O(30)	72.77(15)	71.8(2)
O(31)–Co(1)–O(30)	110.81(13)	107.5(2)
O(50)–Co(1)–O(30)	176.83(14)	179.5(2)
N(42)–Co(2)–O(50)	95.4(2)	94.6(13)
N(42)–Co(2)–N(39)	85.2(3)	87.2(3)
O(50)–Co(2)–N (39)	176.85(15)	178.2(3)
N(42)–Co(2)–O(91)	90.9(2)	93.8(3)
O(50)–Co(2)–O(91)	87.42(15)	86.3(2)
N(39)–Co(2)–O(91)	95.66(17)	93.3(3)
N(42)–Co(2)–O(83)	84.8(2)	85.7(3)
O(50)–Co(2)–O(83)	92.60(15)	93.9(2)
N(39)–Co(2)–O(83)	84.37(16)	86.5(3)
O(91)–Co(2)–O(83)	175.74(18)	179.4(3)
N(42)–Co(2)–O(31)	177.0(2)	176.4(3)
O(50)–Co(2)–O(31)	82.83(13)	84.3(2)
N(39)–Co(2)–O(31)	96.42(19)	93.9(3)
O(91)–Co(2)–O(31)	91.34(15)	89.6(3)
O(83)–Co(2)–O(31)	92.90(15)	91.0(3)
N(22)–Co(3)–N(19)	82.8(4)	88.5(4)
N(22)–Co(3)–O(30)	97.8(3)	95.1(3)
N(19)–Co(3)–O(30)	178.9(2)	176.1(3)
N(22)–Co(3)–O(71)	97.4(3)	92.6(3)
N(19)–Co(3)–O(71)	93.6(2)	93.3(3)
O(30)–Co(3)–O(71)	87.20(16)	88.1(3)
N(22)–Co(3)–O(11)	174.9(3)	176.9(3)
N(19)–Co(3)–O(11)	96.3(3)	93.6(3)
O(30)–Co(3)–O(11)	83.04(16)	82.8(3)
O(71)–Co(3)–O(11)	87.66(17)	89.7(3)
N(22)–Co(3)–O(63)	83.3(3)	86.1(3)
N(19)–Co(3)–O(63)	85.6(2)	84.7(3)
O(30)–Co(3)–O(63)	93.54(17)	94.0(3)
O(71)–Co(3)–O(63)	178.9(2)	177.6(3)
O(11)–Co(3)–O(63)	91.60(18)	91.7(2)

Table 3. Hydrogen bond lengths [Å] and angles [°] for complex **1**.

D–H⋯A	D⋯A	H⋯A	∠D–H⋯A
O100–H101⋯O73	2.759(8)	1.87(6)	167(8)
O100–H102⋯O93	2.818(8)	1.99(7)	157(7)

Description of the Structure of **4**

The structure of **4** is shown in Figure 4. The structure shows the cobalt atom in a distorted octahedral environment bonded to two oxygen atoms of an acetate group and four donor atoms of ligand L⁴. The distortion to the octahedron is primarily caused by the small bite angle to the

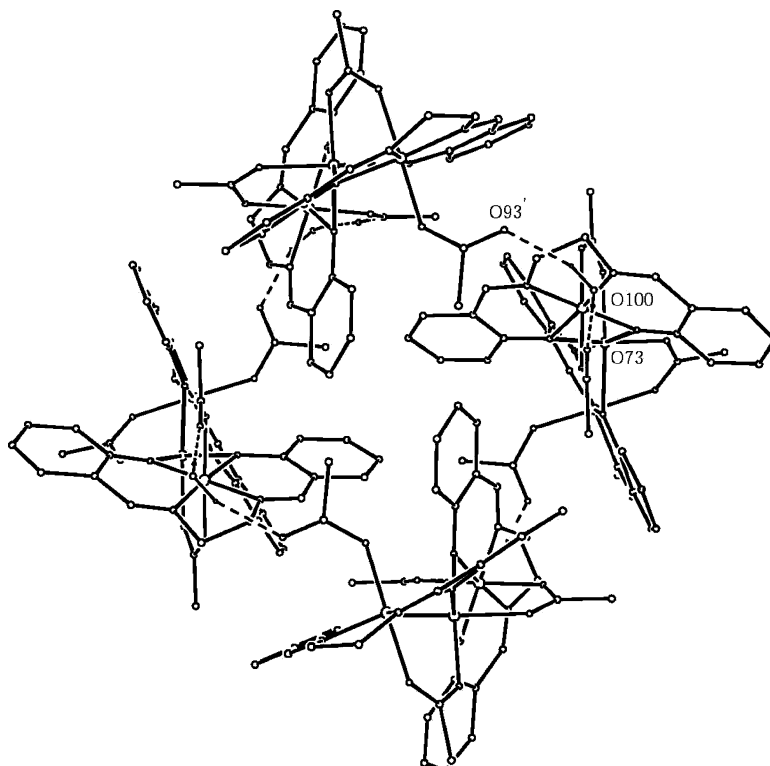


Figure 3. The tetrameric H-bonded structure in **1**.

acetate of $65.9(1)^\circ$. The bond lengths to the acetate are 1.996(1), 1.982(1) Å and for the ligand to oxygen 1.860(1), 1.872(1) Å and to nitrogen 1.935(1), 1.917(1) Å (Table 4).

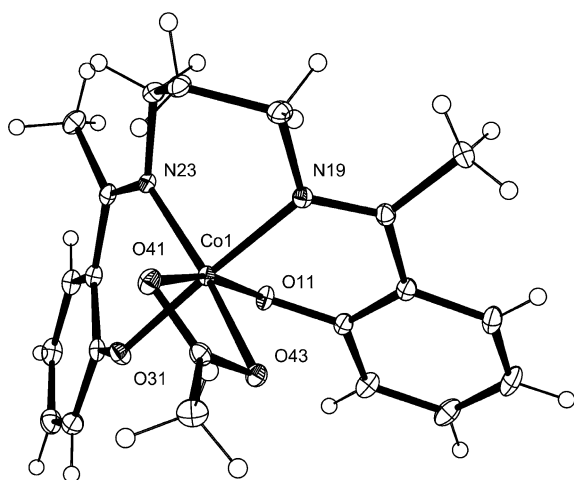


Figure 4. The structure of **4** with ellipsoids at 35% probability.

The conformation of the saturated six-membered ring [Co(1)–N(19)–C(20)–C(21)–C(22)–N(23)–Co(1)] is intermediate between boat and twist-boat with puckering parameters^[16,17] $q_3 = -0.049(2)$, $q_2 = Q = 0.871(1)$, $\theta = 93.2(1)$, $\Phi = 196.22(11)$. The N(19)–Co(1)–N(23) angle is $92.8(1)^\circ$ and is typical of a six-membered chelate ring.^[18] In the octahedral complex of a Salen-type ligand, when it acts as a tetradentate ligand, two different arrangements of four donor atoms around the metal atom is found; one in which the

Table 4. Selected bond lengths [Å] and bond angles [$^\circ$] for compound **4**.

Bond lengths	
Co(1)–O(11)	1.860(1)
Co(1)–O(31)	1.872(1)
Co(1)–O(41)	1.996(1)
Co(1)–O(43)	1.982(1)
Co(1)–N(19)	1.935(1)
Co(1)–N(23)	1.917(1)
Bond angles	
O(11)–Co(1)–O(31)	90.07(5)
O(11)–Co(1)–N(23)	90.60(5)
O(31)–Co(1)–N(23)	90.37(5)
O(11)–Co(1)–N(19)	90.24(5)
O(31)–Co(1)–N(19)	176.83(5)
N(23)–Co(1)–N(19)	92.79(6)
O(11)–Co(1)–O(43)	99.48(5)
O(31)–Co(1)–O(43)	87.67(5)
N(23)–Co(1)–O(43)	169.72(5)
N(19)–Co(1)–O(43)	89.17(5)
O(11)–Co(1)–O(41)	165.04(5)
O(31)–Co(1)–O(41)	86.47(5)
N(23)–Co(1)–O(41)	103.96(5)
N(19)–Co(1)–O(41)	92.43(5)
O(43)–Co(1)–O(41)	65.86(5)

donors occupy the four equatorial positions, the other in which one oxygen is displaced from the equatorial plane, occupying an axial position of the coordination polyhedron.^[19] In the present case, because of the presence of the bidentate acetate, the ligand necessarily assumes the second alternative.

Room-Temperature Magnetic Moment

The effective magnetic moment at room temperature of the two trinuclear complexes (**1** and **2**) was 5.36 and 5.10 BM, which corresponds to the presence of a high-spin Co^{II} in the molecules. The complexes thus contain low spin Co^{III} and high spin Co^{II} , i.e. a $\text{Co}^{\text{III}}(S = 0)\text{--Co}^{\text{II}}(S = 3/2)\text{--Co}^{\text{III}}(S = 0)$ trimer. Complexes **3** and **4** are monomers with only one low-spin Co^{III} and thus are diamagnetic.

Discussion

There are two types of trinuclear linear cobalt complexes with these types of ligands reported in the literature.^[14,20] The first type includes $\text{Co}^{\text{II}}\text{--Co}^{\text{II}}\text{--Co}^{\text{II}}$ complexes^[20] whereas the second variety contains mixed-valence $\text{Co}^{\text{III}}\text{--Co}^{\text{II}}\text{--Co}^{\text{III}}$ complexes.^[14] The structural data reveal that $\text{Co}^{\text{III}}\text{--N}$ and $\text{Co}^{\text{III}}\text{--O}$ distances in Co-Salen-type complexes vary from 1.82–1.88 Å and 1.88–1.91 Å, respectively, whereas those distances in Co-Salpn-type complexes range from 1.92–1.94 Å and 1.86–1.90 Å.^[14]

These variations in bond length have been investigated using Quantum Mechanics methods. The two structures $\text{Co}(\text{Me}_2\text{Salpn})(\text{OAc})$ (**4**) and $\text{Co}(\text{Me}_2\text{Salen})(\text{OAc})$ were investigated with the Gaussian03 program.^[21] The crystal structure of **4** was used as a starting model and that of $\text{Co}(\text{Me}_2\text{Salen})(\text{OAc})$ was built from that by removing a CH_2 moiety and optimisation with molecular mechanics. The two structures were then optimised using Density Functional Theory with the B3LYP methodology in which the Co atom was given the LANL2DZ basis set and the remaining atoms the 6-31+G* basis set. After geometry optimisation, the two structures had equivalent Co–O distances but the Co–N distances were 1.92, 1.92 Å in $\text{Co}(\text{Me}_2\text{Salen})(\text{OAc})$ and 1.95, 1.96 Å in $\text{Co}(\text{Me}_2\text{Salpn})(\text{OAc})$.

Both the X-ray structural data and theoretical calculation indicate that in Salpn-type ligands the $\text{Co}^{\text{III}}\text{--N}$ bond lengths are longer than Salen-type ligands presumably due to the presence of a bulkier trimethylene group between the N atoms causing a weaker ligand field for the Schiff bases derived from 1,3-propanediamine and its derivative. Therefore, it is reasonable to expect that strong field Salen-type ligands can stabilise Co^{III} and thereby form mixed-valence $\text{Co}^{\text{III}}\text{--Co}^{\text{II}}\text{--Co}^{\text{III}}$ complexes easily but with weaker field Salpn-type ligands, the formation of such a mixed-valence complex is unfavourable until another strong field monodentate ligand such as SCN^- or Py is coordinated to the terminal cobalt atoms.^[14b,14c] On the other hand, the Salpn ligands also form either the mononuclear Co^{III} complexes or trinuclear $\text{Co}^{\text{II}}\text{--Co}^{\text{II}}\text{--Co}^{\text{II}}$ complexes depending on the method of preparation and the nature of other co-ligands. The Co^{III} complexes are formed in the aerobic condition and become stable as in the mononuclear complex the chelated Salpn ligand has a shorter Co–O bond length than its phenoxo bridging counterpart and thus can exert stronger crystal field stabilisation energy. The $\text{Co}^{\text{II}}\text{--Co}^{\text{II}}\text{--Co}^{\text{II}}$ complexes are formed when the reaction is carried out under an

inert atmosphere and Co^{II} is stabilised by the weaker field strength of the phenoxo-bridged ligand. Besides the ligand field strength, other factors, e.g. flexibility of the Schiff base and the role of co-ligands should also be taken into consideration for the formation of such complexes with different nuclearities. The Salpn ligand stabilises both the square-planar coordination geometry and the twisted geometry like complex **4** owing to its flexibility. Although the less-flexible Salen ligand also stabilises the meridional coordination geometry, it does not usually stabilise the twisted geometry owing to its structural restriction. Generally, Cu^{II} and Ni^{II} complexes with these kinds of tetradentate Schiff-base ligands are able to coordinate to other metal ions in a di- μ -phenoxo bridging manner as the complex ligands. But Co^{III} , Mn^{III} or Cr^{III} complexes with the same ligands are hard to coordinate to other metal ions in the same manner. However, a second bridging group (e.g. an acetate ion) may reinforce the bridging mode of the phenoxo group of such metallo-ligands to result in the formation of polynuclear complexes such as **1** and **2**. Moreover, the coordination mode of the co-ligands is also important in controlling the nuclearity of the product, especially in the case of flexible ligands L^3 and L^4 . It seems that a monodentate co-ligand (e.g. SCN^- or Py) favours a trinuclear product [R] while a chelating bidentate co-ligand (e.g. CH_3COO^-) gives a mononuclear one.

We investigated these reactions further using Quantum Mechanics methods with the DFT methodology described above. Thus, the enthalpy of the reaction $\text{Co}(\text{OAc})^{2+} + \text{L}^{2-} = \text{Co}(\text{OAc})\text{L}$ was calculated for both $\text{L} = \text{Salen}$ and $\text{L} = \text{Salpn}$ by geometry optimisation of all the structures in the reactions. The starting model for $\text{Co}(\text{OAc})^{2+}$ was obtained by removing L from the $\text{Co}(\text{OAc})\text{L}$ complex and for the ligands was built using the all-*trans* conformations. Values for ΔH of $-68.18 \text{ kcal mol}^{-1}$ for Salen and $-61.50 \text{ kcal mol}^{-1}$ for Salpn were obtained. The significant difference of $6.68 \text{ kcal mol}^{-1}$ suggests that the Salen mononuclear complex is easier to form than the mononuclear Salpn complex. However, as demonstrated in this work, in practice the mononuclear Salpn complex is formed but the mononuclear Salen complex is not as instead it forms the trinuclear complex. This calculation therefore strongly suggests that for Salen, it is the preference for the trimer that is the driving force for its formation rather than any instability in the monomer. However, calculations on the trimers were inconclusive due to convergence problems.

IR and Electronic Spectra

The most important aspects concerning the infrared spectra of the four compounds **1**, **2**, **3** and **4** deal with the possibility of characterising the different coordination modes for the acetate ligand to a transition metal, which is usually detected by the differences ($\Delta\nu$) in the antisymmetric $\nu_{\text{asym}}(\text{COO})$ and symmetric stretching frequencies $\nu_{\text{sym}}(\text{COO})$.^[22] The infrared spectrum of complex **1** displays several intense bands at 1650, 1597, 1447 and 1425 cm^{-1} and

they are assigned to $\nu(\text{COO}^-)$ frequencies. The appearance of four bands corroborates the presence of two types of acetate groups. Separations of 150 cm^{-1} (between the bands at 1597 and 1447 cm^{-1}) and 225 cm^{-1} (between 1650 and 1425 cm^{-1}) suggest their assignment to bridging and unidentate carboxylate coordinations, respectively (163 cm^{-1} for the free acetate ion). A similar structure is indicated for complex **2** because of the similarity of the pattern of the IR spectrum.

Two intense bands at 1586 and 1474 cm^{-1} in the IR spectrum of complex **3** are assigned to $\nu(\text{COO}^-)$ frequencies. Separations between frequencies of 112 cm^{-1} indicate the chelating bidentate coordination of the acetate moiety.

In the IR spectra of all four complexes a distinct band due to the azomethine ($\text{C}=\text{N}$) group at $1649\text{--}1573\text{ cm}^{-1}$ is routinely seen and the red shift of this $\text{C}=\text{N}$ absorption of about 15 cm^{-1} on going from the free ligands to the complexes suggests the weak π -accepting ability of the coordinated ligands. A broad band around 3400 cm^{-1} indicates the presence of an H_2O molecule in the crystals of **1** and **2**.

The electronic spectra of **1** and **2** display one low energy absorption band at 703 and 547 nm , respectively, attributable to a transition in the visible region of a low-spin cobalt(III) in octahedral geometry, obscuring the transitions of the divalent metal ions. Bands from Co^{II} are Laporte-forbidden transitions and are assumed to be too weak to be visible. The electronic spectra of **3** and **4** also contain low-energy bands at 658 and 569 nm .

Luminescence Studies

The spectroscopic data of the four complexes and that for the free ligands in acetonitrile solution are listed in Table 5. These are assigned to intraligand $^1(\pi\text{--}\pi^*)$ fluorescence.^[23]

Table 5. Photophysical data for complexes **1–4** and also for the free ligands.

Sample	Absorption	Emission
1	364	517
2	355	502
3	371	523
4	359	506
H_2Salen	406	472
H_2Salpn	398	454
$\text{H}_2\text{Me}_2\text{Salen}$	410	473
$\text{H}_2\text{Me}_2\text{Salpn}$	414	480

Conclusions

In this study, it has been shown that the mixed oxidation state tricobalt(III/II/III) complex is produced when a Salen-type Schiff base is allowed to react with Co^{II} acetate in the presence of air. On the other hand, Salpn-type Schiff bases yield mononuclear Co^{III} complexes under the same conditions. These examples thus demonstrate for the first time that the methylene spacer in the diamine fragment of the

Schiff base can regulate the nuclearity and oxidation state of the exhaustively studied cobalt–Schiff base complexes.

Experimental Section

Materials and Methods: All chemicals were of reagent grade and used without further purification. Elemental analysis (C, H, N) was performed with a Perkin–Elmer 240C elemental analyser. IR spectra ($4500\text{--}500\text{ cm}^{-1}$) were recorded as KBr pellets with a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile ($1200\text{--}350\text{ nm}$) were recorded with a Hitachi U-3501 spectrophotometer. The magnetic susceptibility measurements were performed with an EG & PAR vibrating sample magnetometer, model 155 at room temperature and diamagnetic corrections were made using Pascal's constants.

Synthesis of the Ligands: The ligands H_2L^1 and H_2L^2 were synthesised by condensation of 1,2-diaminoethane with salicylaldehyde or 2-hydroxyacetophenone, respectively, in dry methanol following the literature method.^[24] The ligands H_2L^3 and H_2L^4 were prepared in the same way using 1,3-diaminopropane instead of 1,2-diaminoethane.

Synthesis of Complexes 1 and 2: To prepare complexes **1** and **2**, a methanol solution (20 mL) of cobalt(II) acetate tetrahydrate (3 mmol, 747 mg) was added to the ligand solution of H_2L^1 (2 mmol, 536 mg) and H_2L^2 (2 mmol, 624 mg), respectively, and the mixture was stirred vigorously for 3 h. Deep brown precipitates of complexes **1** and **2** were separated out after 2 days and were collected by filtration. Diffraction quality single crystals were obtained after a few days by slow evaporation of the dark brown dichloromethane solution of the compounds in an open atmosphere.

Compound 1: Yield 0.812 g (82%). $\text{C}_{40}\text{H}_{45}\text{Co}_3\text{N}_4\text{O}_{14.5}$ (990.59): calcd. C 50.81, H 4.26, N 5.93; found C 51.23, H 4.93, N 6.01. UV/Vis (acetonitrile): λ_{max} (ϵ_{max} , $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) = 703 (1879), 364(8058) nm. Magnetic moment $\mu = 5.36\text{ BM}$.

Compound 2: Yield 0.877 g (86%). $\text{C}_{44}\text{H}_{50}\text{Co}_3\text{N}_4\text{O}_{13}$ (1019.67): calcd. C 52.76, H 4.83, N 5.59; found C 52.90, H 5.74, N 6.31. UV/Vis (acetonitrile): λ_{max} (ϵ_{max} , $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) = 547 (1159), 355 (5185) nm. Magnetic moment $\mu = 5.10\text{ BM}$.

Synthesis of Complexes 3–4: Complexes **3** and **4** were prepared by adding a methanol solution (20 mL) of cobalt(II) acetate hexahydrate (2 mmol, 498 mg) into the methanol solution of H_2L^3 (2 mmol, 564 mg) and H_2L^4 (2 mmol, 620 mg), respectively, and stirring vigorously. Brown precipitates separated out immediately and were collected by filtration. Diffraction quality single crystals of **4** were obtained after a few days by slow evaporation of a brown dichloromethane solution in a refrigerator, but it was not possible to isolate suitable single crystals of **3** for X-ray diffraction.

Compound 3: Yield 0.34 g (85%). $\text{C}_{19}\text{H}_{19}\text{CoN}_2\text{O}_4$ (398.07): calcd. C 57.29, H 4.81, N 7.03; found C 57.18, H 4.56, N 7.32. UV/Vis (acetonitrile): λ_{max} (ϵ_{max} , $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) = 658 (1055), 371 (8045) nm. MS: m/z (%) = 400.08 [M^+], 401.09 [$\text{M} + 1$]⁺, 402.09 [$\text{M} + 2$]⁺. Magnetic moment, diamagnetic.

Compound 4: Yield 0.374 g (88%). $\text{C}_{21}\text{H}_{23}\text{CoN}_2\text{O}_4$ (426.34): calcd. C 59.16, H 5.44, N 6.57; found C 59.24, H 5.56, N 6.52. UV/Vis (acetonitrile): λ_{max} (ϵ_{max} , $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) = 569 (972), 359 (9876) nm. Magnetic moment, diamagnetic.

X-ray Crystallography: Crystal data for all the three crystals are given in Table 6. Crystal data for the three crystals were measured

Table 6. Crystal data for compounds **1**, **2** and **4**.

	1	2	4
Formula	C ₄₀ H ₄₅ Co ₃ N ₄ O _{14.5}	C ₄₄ H ₅₀ Co ₃ N ₄ O ₁₃	C ₂₁ H ₂₃ CoN ₂ O ₄
Formula weight	990.59	1019.67	426.34
Temperature [K]	150	150	150
Crystal system	tetragonal	monoclinic	triclinic
Space group	<i>I</i> 4	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	23.426(1)	17.989(3)	8.604(1)
<i>b</i> [Å]	23.426(1)	11.664(2)	10.071(1)
<i>c</i> [Å]	16.328(1)	21.578(4)	11.311(1)
α [°]	(90)	(90)	99.64(1)
β [°]	(90)	97.59(1)	94.80(1)
γ [°]	(90)	(90)	106.33(1)
<i>V</i> [Å ³]	8960.0(8)	4487.8(1)	918.4(2)
<i>Z</i>	4	4	2
<i>D</i> _{calcd.} [mgm ⁻³]	1.469	1.509	1.542
μ [mm ⁻¹]	1.17	1.17	0.97
<i>F</i> (000)	4080	2108	444
Crystal size [mm]	0.05 × 0.05 × 0.30	0.03 × 0.03 × 0.22	0.05 × 0.05 × 0.30
Total reflections	30785	30745	6514
Independent reflections	13073	13070	5141
<i>R</i> _{int}	0.060	0.205	0.014
Collected reflections [<i>I</i> > 2σ(<i>I</i>)]	5144	1975	4304
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1543, 0.1302	0.3319, 0.2175	0.0391, 0.0877
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0544, 0.1142	0.0793, 0.1901	0.0314, 0.0861

with Mo-*K*_α radiation at 150 K on an Oxford Diffraction X-Calibur CCD system; 321 frames were measured with counting times of 10 s, 50 s and 2 s, respectively, for **1**, **2** and **4**. Data analysis was carried out with the CRYSTALIS program^[25] to provide 13073, 13070 and 5141 independent reflections, respectively. The structures were solved by direct methods with the SHELXS97 program.^[26] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2-times those of the atom to which they were attached. Empirical absorption corrections were carried out with the ABSPACK program.^[27] The structures were refined on *F*² using SHELXL97^[26] to *R*1 = 0.0544, 0.0793, 0.0314 and *wR*2 = 0.1142, 0.1901, 0.0861 for 5144, 1975, 4304 reflections with *I* > 2σ(*I*) for **1**, **2** and **4**, respectively.

CCDC-656434 (for **1**), -656435 (for **2**) and -656436 (for **4**) 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.

Acknowledgments

We like to thank the Engineering and Physical Sciences Research Council (EPSRC) and the University of Reading for funds for the Marresearch Image Plate and Oxford Diffraction CCD systems.

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Received: September 21, 2007

Published Online: February 13, 2008