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Synthesis, characterization, molecular structure and self-assembly of some cobalt(III) complexes derived from diacetyl- and benzil bisaroylhydrazones

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ABSTRACT

Cobalt(III) complexes of the general formula $[Co(HL^1-R)(L^1-R)]$, $[Co(HL^2-R)(L^2-R)]$ and $[Co(HL^1-R)_2]Cl$, where H_2L^1-R and H_2L^2-R referred respectively to diacetyl and benzil bis(aroylhydrazone), have been prepared and characterized by IR, electronic, ESI and ¹H NMR spectral measurements. The bisaroylhydrazone ligand in these complexes acts either as mononegative N_2O tridentate, $[HL^{1,2}-R]^-$, or dinegative N_2O tridentate, $[L^{1,2}-R]^{2-}$. Coordination occurs via the two diimine nitrogens and the deprotonated enolimine oxygen of one aroylhydrazone moiety, leaving the other one uncoordinated. The X-ray crystal structures of $[Co(HL^2-CH_3)(L^2-CH_3)]$ and $[Co(HL^1-R)_2]Cl$ (R = H, CH_3) show that the molecular units are assembled into dimers through π - π stacking and hydrogen-bonded interactions respectively in the neutral and cationic complexes. Both types of dimers are linked together giving linear chains which in turn are interconnected to produce layers. These layers are further assembled with each other in $[Co(HL^2-CH_3)(L^2-CH_3)]$ and $[Co(HL^1-H)_2]Cl$ to generate three-dimensional frameworks, while in the cationic complex $[Co(HL^1-CH_3)_2]Cl$, the molecular units form chains of dimers with a one-dimensional tubular structure.

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1. Introduction

Condensation of α -dicarbonyl compounds with aroylhydrazines affords the corresponding bisaroylhydrazones (Scheme 1). The ligating properties of these bisaroylhydrazones have attracted considerable research interest due to their versatility in binding to metal ions in different ways. They can function as dinegative tetradentate N₂O₂ ligands, coordinating via the diimine nitrogens and the two enolimine oxygens, forming neutral complexes with divalent metal ions. The increased electron delocalization in the dianion produces a square planar N2O2 environment, well designed for Ni(II) and Cu(II) ions which have a strong tendency to form square planar complexes [1–3]. In fact, neutral [Ni(L)] complexes have been synthesized with diacetyl- and benzil bis(benzoylhydrazone) and their X-ray crystal structures [2,3] have shown that the bishydrazone ligand acts as a dinegative tetradentate N₂O₂ ligand, forming three 5-membered chelating rings. Using the same argument for mononuclear octahedral complexes, the doubly deprotonated N₂O₂ bishydrazone would lie in the equatorial plane [3,4–7]. The X-ray structure analysis of a nickel diacetyl bis (aroylhydrazone) bisimidazole adduct [3] and a trans diammine

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diacetylbis(aroylhydrazonato)cobalt(III) cation [8] indicates a distorted octahedral geometry with the bisaroylhydrazone in the equatorial plane and the two bases in the axial positions. Moreover, X-ray diffraction studies of a series of organotin complexes with benzil bis(benzoylhydrazone) revealed that in the distorted octahedral arrangement the ligand behaves as a tetradentate N₂O₂ dianion in the equatorial plane and the organic groups are positioned in the axial sites [9]. In the case of a 5-coordinate mononuclear Cu(II) complex with diacetyl bis(benzoylhydrazone), CuLMeOH, the X-ray crystal structure indicated that the Cu(II) ion is in a square pyramidal environment where the dianionic N₂O₂ tetradentate ligand occupies the basal plane, while the methanol oxygen atom lies at the apex [10]. Another mode of coordination is exhibited by the base adduct of nickel diacetyl bis (benzovlhvdrazone) with 1.10-phenanthroline, where the X-ray crystal structure revealed that the bishydrazone ligand acts as an anionic N₂O tridentate ligand, leaving one enolimide oxygen atom uncoordinated [11]. This is different from the monobase adduct of nickel phenylglyoxal bisaroylhydrazone with imidazole in which the ligand functions as a dinegative ligand with N₂O donor atoms, namely the imine nitrogen, enolimine oxygen and hydrazine nitrogen, forming two 5- and 6-membered rings [3]. In a more peculiar way, the X-ray crystal structure of dimeric $[Cu_2(\mu-L)_2]$ reveals that diacetyl bis(benzoylhydrazone) acts as bridging ligand. Each Cu(II)







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Scheme 1.

is in a distorted square planar N₂O₂ environment formed by two halves of two different ligand molecules, giving rise to a double helical structure [12]. An unusual mode of chelation of diacetyl bis(benzoylhydrazone) is shown in a dinuclear dimeric neutral Pd(II) complex, where the ligand behaves as dianionic N₃O tetradentate [13]. Each metal center is coordinated in a square planar structure to two imine nitrogens and one deprotonated enolic oxygen belonging to one ligand and the deprotonated amide nitrogen of the other ligand. The versatility of benzil bis(benzoylhydrazone) has also been demonstrated in the various molecular architectures adopted by the binuclear $[Pb(L)]_2$ and $[Cd(L)]_2$ complexes as well as the trinuclear $[Zn(L)]_3$ and $[Cu(L)]_3$ helicates [2]. In the binuclear complexes, each metal center is in a 5-coordinate environment formed from one tetradentate N2O2 dianion and the oxygen of another ligand acting as bridge in a strongly TBP structure. However in the trinuclear complexes, each bishydrazone is pentadentate N₃O₂, where it acts as tridentate N₂O towards one metal center via the imine nitrogen, the oxygen of one arm and the deprotonated amide nitrogen of the other arm, and also functions as bidentate NO, being bound to another metal center via the remaining imine nitrogen and oxygen of the bishydrazone ligand [2].

The various modes of chelation and the flexibility of diacetyland benzil bis(aroylhydrazone) stimulated our attention to investigate the ligating behavior and the coordination sites of these ligands with regard to the octahedral geometry of cobalt(III) ions. In this context, cationic $[Co(HL^1-R)_2]CI$ (R = H and CH₃) as well as neutral $[Co(HL^1-R)(L^1-R)]$ (R = H, CH₃, CH₃O, Cl) and $[Co(HL^2-R)(L^2-R)]$ (R = CH₃ and Cl) bisligand Co(III) complexes have been synthesized and characterized. The X-ray molecular and supramolecular structures of $[Co(HL^1-H)_2]CI$, $[Co(HL^1-CH_3)_2]CI$ and $[Co(HL^2-CH_3)(L^2-CH_3)]$ will be discussed.

2. Experimental

2.1. Materials

Diacetyl and benzil were purchased from Aldrich and were used as received. Hydrazine hydrate (99%), cobalt(II) acetate tetrahydrate and cobalt(II) chloride hexahydrate (BDH) were used without further purification. The aroylhydrazines were prepared as previously described [14] by the hydrazinolysis of carboxylic methyl esters in methanol. The diacetyl and benzil bis(aroylhydrazone) were prepared using the same procedure previously described [1–3].

2.2. Preparation of the Co(III) cationic complexes $[Co(HL^1-R)_2]Cl$ ($R = H, CH_3$)

A hot solution of cobalt(II) chloride hexahydrate (1.0 mmol) in methanol (50 ml) was added dropwise to a stirred suspension of the bis(aroylhydrazone), $H_2L^{1}-R$ (R = H, CH₃), (2.2 mmol) in

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methanol (50 ml). The reaction mixture was heated under reflux with constant stirring for 2 h, during which time a stream of air was bubbled through the mixture to ensure the complete oxidation of any Co(II) intermediates that may have been formed in solution. The resulting brown solution was filtered to separate any insoluble impurities, and then evaporated to half its volume. The brown Co(III) complex, which separated on cooling to room temperature, was isolated by filtration, washed with diethyl ether, then dried in air.

2.2.1. $[Co(HL^1-H)_2]Cl(1)$

Yield 42%. Anal. Calc. for $C_{36}H_{34}N_8O_4ClCo: C, 58.66; H, 4.65; N, 15.20. Found: C, 58.45; H, 4.51; N, 14.92%. IR (KBr, cm⁻¹): 3080 <math>v(N-H)$, 1675 amide I v(C=O), 1595 v(C=N-N=C), 1550, v(N=C-C=N), 1533 amide II [δ (N-H) + v(C-N)], 1322 amide III v(C-N); UV-Vis. (methanol, saturated solution, λ_{max}/nm): 290, 350sh, 403, 520. ESI (+) MS (DMF/CH₃OH) *m*/*z* Calcd. (RA): 380.1 (379.2832) (75.6), $[Co(L^1-H)]^{1+}$; 452.0 (452.3683) (6.0), $[Co(L^1-H)(DMF)]^{1+}$; 525.0 (525.4721) (5.2) $[Co(L^1-H)(DMF)_2]^{1+}$; 647.2 (645.6025) (70.0) $[\{Co_2(L^1-H)_3\}(DMF)_2(MeOH)_2 + 2H]^{2+}$; 701.2 (701.6490) (70.4) $[Co(HL^1-H)_2]^{1+}$; 759.0 (759.5744) (5.0) $[\{Co(L^1-H)\}_2 + H]^{1+}$. ¹H NMR (CDCl₃, ppm): 2.63 (s, 6H, 2CH₃-C=N), 2.67 (s, 6H, 2CH₃-C=N), 7.35 (m, 4H, aromatic), 7.45 (m, 6H, aromatic), 7.57 (s, 2H, aromatic), 8.00 (m, 4H, aromatic), 8.13 (m, 4H, aromatic), 11.90 (s, 2H, N-H).

2.2.2. [Co(HL¹-CH₃)₂]Cl (2)

Yield 40%. *Anal.* Calc. for $C_{40}H_{42}N_8O_4ClCo: C, 60.57; H, 5.34; N, 14.13. Found: C, 60.34; H, 5.04; N, 13.85%. IR (KBr, cm⁻¹): 3080 <math>v(N-H)$, 1670 amide I v(C=O), 1560 v(C=N-N=C), 1555 v(N=C-C=N), 1533 amide II [δ (N–H) + v(C–N)], 1375s, 1325s amide III v(C-N); UV–Vis. (methanol, saturated solution, λ_{max}/nm): 300, 355sh, 400, 525. ESI (+) MS (DMF/CH₃OH) *m/z* Calcd. (RA): 407.0 (407.3369) (90) [Co(L¹–CH₃)]¹⁺; 480.2 (480.4312) (5.50) [Co(L¹–CH₃)(DMF)]¹⁺; 553.0 (553.5256) (4.20) [Co(L¹–CH₃)(DMF)₂]¹⁺; 686.2 (687.6829) (55.63) [{Co₂(L¹–CH₃)₂]¹⁺; 814.0 (815.6815) (6.2) [{Co(HL¹–CH₃)₂]¹⁺. ¹H NMR (CDCl₃, ppm): 2.17 (s, 6H, 2CH₃–C=N), 2.45 (s, 6H, 2CH₃–C=N), 2.30 (s, 12H, 4 *p*-CH₃), 7.26 (8H, aromatic), 7.78 (4H, aromatic), 8.10 (4H, aromatic), 11.80 (s, 2H, NH).

2.3. Preparation of neutral $[Co(HL^1-R)(L^1-R)]\cdot nH_2O(R = H, CH_3, CH_3O, Cl)$ and $[Co(HL^2-R)(L^2-R)]\cdot nH_2O(R = CH_3, Cl)$ complexes

The neutral cobalt(III) complexes $[Co(HL^1-R)(L^1-R)] \cdot nH_2O(R = C_6H_5, p-CH_3C_6H_4, p-CH_3OC_6H_4, p-CIC_6H_4)$ and $[Co(HL^2-R)(L^2-R)] \cdot nH_2O(p-CH_3C_6H_4, p-CIC_6H_4)$ were prepared using the same procedure described for the preparation of the cationic complexes (Section 2.2), but using cobalt(II) acetate tetrahydrate instead of cobalt(II) chloride hexahydrate.

2.3.1. $[Co(HL^1-H)(L^1-H)]$ (3)

Yield 42%. Anal. Calc. for $C_{36}H_{33}N_8O_4Co: C, 61.71; H, 4.75; N, 15.99.$ Found: C, 61.10; H, 4.744; N, 15.64%. IR (KBr, cm⁻¹): 3430m v(O–H), 1595s v(C=N–N=C), 1549s v(N=C–C=N), 1376vs, 1298m amide III v(C–N), 967m v(N–N). UV–Vis. (DMF, λ_{max}/nm (log ε)): 310(4.64), 404(4.41), 645(sh). ESI (+) MS (DMF/CH₃OH) m/z Calcd. (RA): 380.1 (379.2832) (100) [Co(L¹–H)]¹⁺; 452.0 (452.3683) (7.41) [Co(L¹–H)(DMF)]¹⁺; 525.0 (525.4721) (6.21) [Co(L¹–H)(DMF)₂]¹⁺; 647.2 (645.6025) (60.45) [{Co₂(L¹–H)₃} (DMF)₂(MeOH)₂ + 2H]²⁺; 701.2 (701.6490) (45.19) [Co(HL¹–H) (L¹–H) + H]¹⁺; 760.0 (759.5744) (5.20) [{Co(L¹–H)}₂ + H]¹⁺. ¹H NMR (CDCl₃, ppm): 2.22 (s, 6H, 2CH₃–C=N), 2.52 (s, 6H, 2CH₃–C=N), 7.37 (m, 12H, aromatic), 7.90 (s, 4H, aromatic), 8.17 (s, 4H, aromatic), 11.89 (s, 1H, OH).

2.3.2. $[Co(HL^1-CH_3)(L^1-CH_3)] \cdot H_2O(4)$

Yield 38%. Anal. Calc. for $C_{40}H_{43}N_8O_5Co: C, 62.01; H, 5.59; N, 14.46. Found: C, 62.18; H, 5.492; N, 14.31%. IR (KBr, cm⁻¹): 3438m v(O-H), 1605s v(C=N-N=C), 1535s v(N=C-C=N), 1375vs, 1301m amide III v(C-N), 969m v(N-N). UV-Vis. (DMF, <math>\lambda_{max}/nm$ (log ε)): 313(4.58), 401(sh), 500(sh), 634(sh). ESI (+) MS (DMF/ CH₃OH) *m*/*z* Calcd. (RA): 407.0 (407.3369) (100) [Co(L¹-CH₃)]¹⁺; 480.2 (480.4312) (8.50) [Co(L¹-CH₃)(DMF)]¹⁺; 553.0 (553.5256) (5.40) [Co(L¹-CH₃)(DMF)₂]¹⁺; 686.2 (687.6829) (55.63) [{Co₂(L¹-CH₃)₃}(DMF)₂(MeOH)₂ + 2H]²⁺; 757.2 (757.7563) (60.20) [Co(HL¹-CH₃)(L¹-CH₃) + H]¹⁺; 815 (815.6815) (5.10) [{Co(L¹-CH₃)₂ + H]¹⁺. ¹H NMR (CDCl₃, ppm): 2.18 (s, 6H, 2CH₃-C=N), 2.49 (s, 6H, 2CH₃-C=N), 2.38 (s, 12H, 4 *p*-CH₃), 7.26 (8H, aromatic), 7.78 (4H, aromatic), 8.05 (4H, aromatic); 11.88 (s, 1H, OH).

2.3.3. $[Co(HL^1 - OCH_3)(L^1 - OCH_3)]$ (5)

Yield 38%. Anal. Calc. for $C_{40}H_{41}N_8O_8Co: C, 58.54$; H, 5.04; N, 13.65. Found: C, 57.98; H, 5.019; N, 13.35%. IR (KBr, cm⁻¹): 3432m v(O-H), 1603s v(C=N-N=C), 1558 v(N=C-C=N), 1373vs, 1307s amide III v(C-N), 967m v(N-N). UV–Vis. (DMF, λ_{max}/nm (log ε)): 340(4.59), 493(sh), 639(sh). ESI (+) MS (DMF/CH₃OH) m/z Calcd. (RA): 439.2 (439.3356) (100) [Co(L¹–OCH₃)]¹⁺; 512.0 (512.4299) (7.8) [Co(L¹–OCH₃)(DMF)]¹⁺; 584.2 (585.5244) (6.5) [Co(L¹–OCH₃)(DMF)₂]¹⁺; 735.0 (735.6810) (60.0) [{Co₂(L¹–O CH₃)₃}(DMF)₂(MeOH)₂ + 2H]²⁺; 821.0 (821.7539) (35.3) [Co(HL¹–OCH₃)(L¹–OCH₃) + H]¹⁺; 878.9 (879.6790) (8.9) [{Co(L¹–OCH₃)}₂ + H]¹⁺. ¹H NMR (CDCl₃, ppm): 2.20 (s, 6H, 2CH₃C=N), 2.49 (s, 6H, 2CH₃C=N), 3.91 (s, 12H, 4p–OCH₃), 6.89 (s, 8H, aromatic), 7.86 (s, 4H, aromatic), 8.14 (s, 4H, aromatic), 11.75 (s, 1H, OH).

2.3.4. $[Co(HL^1-Cl)(L^1-Cl)] \cdot H_2O(\mathbf{6})$

Yield 48%. Anal. Calc. for $C_{36}H_{31}N_8O_5Cl_4Co: C, 50.49; H, 3.65; N, 13.08. Found: C, 50.55; H, 3.613; N, 12.87%. IR (KBr, cm⁻¹): 3428m <math>v(O-H)$, 1593s v(C=N-N=C), 1545 v(N=C-C=N), 1377vs, 1293m amide III v(C-N), 970m v(N-N). UV–Vis. (DMF, λ_{max}/nm (log ε)): 316(4.55), 434(sh). ESI (+) MS (DMF/CH₃OH) m/z Calcd. (RA): 448.1 (448.1728) (100) $[Co(L^1-CI)]^{1+}; 521.2$ (521.2579) (11.85) $[Co(L^1-CI)(DMF)]^{1+}; 751.2$ (750.4388) (93.28) $[\{Co_2(L^1-CI)_3\}$ (DMF)₂(MeOH)₂ + 2H]²⁺; 837.1 (839.4282) (11.00) $[Co(HL^1-CI)(L^1-CI) + H]^{1+}; 897.0$ (897.3548) (6.10) $[\{Co(L^1-CI)\}_2 + H]^{1+}.$

2.3.5. $[Co(HL^2-CH_3)(L^2-CH_3)]$ (7)

Yield 53%. Anal. Calc. for $C_{60}H_{49}N_8O_4Co:$ C, 71.71; H, 4.91; N, 11.15. Found: C, 71.37; H, 4.862; N, 11.02%. IR (KBr, cm⁻¹): 3431m ν (O–H), 1583m ν (C=N–N=C), 1442s, 1375vs, 1269m amide III ν (C–N), 1020m ν (N–N). UV–Vis. (DMF, $\lambda_{max}/nm (log <math>\varepsilon$)): 351(sh). ESI (+) MS (DMF/CH₃OH) *m/z* Calcd. (RA): 531.5 (531.4784) (100) [Co(L²–CH₃)]¹⁺; 605.4 (604.5635) (28.57) [Co(L²–CH₃) (DMF)]¹⁺; 677.5 (677.6486) (44.36) [Co(L²–CH₃)(DMF)₂]¹⁺; 873.5 (873.8428) (44.78) [{Co₂(L²–CH₃)₃}(DMF)₂(MeOH)₂ + 2H]²⁺; 1005.5 (1006.041) (67.67) [Co(HL²–CH₃)(L²–CH₃) + H]¹⁺. ¹H NMR (CDCl₃, ppm): 2.38 (d, 12H, 4*p*-CH₃), 7.17 (m, 28H, aromatic), 7.26 (s, 3H, aromatic), 8.08 (s, 5H, aromatic), 12.61 (s, 1H, OH).

2.3.6. $[Co(HL^2-Cl)(L^2-Cl)] \cdot 1.5H_2O(\mathbf{8})$

Yield 55%. Anal. Calc. for $C_{56}H_{37}N_8O_4Cl_4Co \cdot 1.5H_2O$: C, 60.39; H, 3.62; N, 10.06. Found: C, 59.95; H, 3.390; N, 10.05. IR (KBr, cm⁻¹): 3440w v(O-H), 1582m, 1526vs v(C=N-N=C), 1380vs, 1326s amide III v(C-N), 940m v(N-N). UV–Vis. (DMF, λ_{max}/nm (log ε)): 341(4.61), 399(sh), 443(sh), 465(sh). ESI (+) MS (DMF/CH₃₋OH) m/z Calcd. (RA): 572.0 (572.3144) (100) [Co(L²–CI)]¹⁺; 645.3 (645.3995) (3.70) [Co(L²–Cl)(DMF)]¹⁺; 934.0 (934.1423) (5.0) [Co₂(L²–Cl)₃(DMF)₂(MeOH)₂ + 2H]²⁺; 1087.0 (1087.7114) (53.38) [Co(HL²–Cl)(L²–Cl) + H]¹⁺; 1145.2 (1146.6459) (5.0) [{Co(L²–Cl)}₂ + H]¹⁺. ¹H NMR (CDCl₃, ppm): 7.31 (d, 28H, aromatic), 7.71 (s, 4H, aromatic), 8.15 (s, 4H, aromatic), 12.75 (s, 1H, OH).

2.4. Physical measurements

The infrared spectra were recorded on a Perkin-Elmer 1430 Data system and/or a Perkin-Elmer (FT-IR) Paragon 1000 PC spectrophotometer. Solid samples were examined as KBr discs. The UV–Vis absorption spectra were recorded on a V-530 Jasco, UV–Vis recording spectrophotometer, using 10 mm quartz cells and/ or a double beam ratio recording Lambda 4B Perkin-Elmer spectrophotometer. ¹H NMR spectra were recorded on a Bruker WM 300 using tetramethylsilane (TMS) as an internal standard. ESI mass spectra were recorded on an Esquire-LC from Bruker Daltonic Nebulizer 10 psi (dry gas 8 L min⁻¹, dry temperature 250 °C). The theoretical isotopic distribution patterns for ionic species were generated using the ISOFORM program and/or Sheffield University Chemputer software [15]. Elemental analyses (C, H, N) were performed at the Micro analytical Laboratory, at the Institut für Organische Chemie Technische Universität, Darmstadt, Germany.

X-ray diffraction data for complexes **1** and **2** were collected on a Nonius CADY diffractometer, while diffraction data for **7** were collected on an XCalibur diffractometer. Graphite monochromated Mo K α radiation ($\lambda = 0.71013$ Å) was used in all cases. The structures were solved by direct methods with SHELXS-97 [16] and refined with full-matrix least squares on F^2 using SHELXL-97 [16]. Drawings of the molecules were produced with ORTEP3 [17] OF PLATON [18]. Crystal data and details concerning data collection and structure refinement for $[Co(HL^1-H)_2]Cl$ (1), $[Co(HL^1-CH_3)_2]Cl$ (2) and $[Co(HL^2-CH_3)(L^2-CH_3)]$ (7) are collected in Table 1. Selected bond distances and bond angles for both (1) and (2) are listed in Table 2, while those of (7) are given in Table 3.

3. Results and discussion

3.1. Synthesis and characterization

The reaction of cobalt(II) acetate tetrahydrate with two equivalents of diacetyl bis(aroylhydrazone), H_2L^1 –R (R = H, CH₃, CH₃O, Cl), and benzil bis(aroylhydrazone), H_2L^2-R (R = CH₃, Cl), in methanol followed by air oxidation afforded the neutral bisligand Co(III) complexes $[Co(HL^1-R)(L^1-R)] \cdot nH_2O$ (R = H, CH₃, CH₃O, Cl) and $[Co(HL^2-R)(L^2-R)]$ (R = CH₃, Cl) respectively. On using Co(II) chloride, the reaction proceeded with the formation of the cationic bisligand complexes, $[Co(HL^1-R)_2]Cl(R = H and CH_3)$. Both the neutral and cationic Co(III) complexes are diamagnetic and display d-d spectra diagnostic of distorted octahedral Co(III) complexes. The solution spectra of both the neutral $[Co(HL^1-R)(L^1-R)] \cdot nH_2O$ $(R = H, CH_3, CH_3O, Cl)$ and $[Co(HL^2-R)(L^2-R)]$ $(R = CH_3, Cl)$ and cationic $[Co(HL^1-R)_2]Cl$ (R = H and CH₃) complexes in DMF are more or less similar and display absorptions at 350-400, 480-500 and 630–650 nm due to different transitions from singlet ¹A_{1g} to higher ${}^{1}T_{1g}$ and ${}^{1}T_{2g}$ states [19].

The IR spectra of the neutral complexes $[Co(HL^1-R)(L^1-R)] \cdot nH_2O$ (R = H, CH₃, CH₃O, Cl and $[Co(HL^2-R)(L^2-R)]$ (R = CH₃, Cl) lack absorptions which could be attributed to v(N-H), amide I [v(C=O)] and amide II $[\delta(NH) + v(C-N)]$, but show a series of absorption bands at 3430–3440, 1610–1590 and 1550–1540 cm⁻¹ respectively due to hydrogen bonded v(OH), oxazine v(C=N-N=CO) and diimine v(N=C-C=N) stretching vibrations of the protonated enolimine aroylhydrazone residue. Different from the spectra of the neutral complexes, the IR spectra of the cationic complexes show absorption bands at 3060, 1673 and 1533 cm⁻¹ respectively due to v(N-H), amide I [v(C=O)] and amide II $[\delta(NH) + v(C-N)]$ of the ketoamide aroylhydrazone residue (Scheme 2-i). The spectra also show intense absorptions at 1595 and 1550 cm⁻¹ respectively due to v(C=N-N=CO) and diimine v(N=C-C=N) stretching vibrations of the deprotonated enolimine aroylhydrazone residue.

Table 1

Crystal data and structure refinement for $[Co(HL^1-H)_2]CI(1)$, $[Co(HL^1-CH_3)_2]CI(2)$ and $[Co(HL^2-CH_3)(L^2-CH_3)(7)$.

	(1)	(2)	(7)
Empirical formula	$C_{36}H_{34}CICoN_8O_4$	C40H42ClCoN8O4	C ₆₀ H ₄₉ CoN ₈ O ₄
Formula weight	735.11	793.20	1005.00
T (K)	299(2)	303(2)	293(2)
λ (Å)	0.71093	1.54180	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	P21/n	C2/c	ΡĪ
Unit cell dimensions			
a (Å)	11.358(4)	24.167	12.4715(8)
b (Å)	12.837(5)	14.082(2)	12.7650(8)
<i>c</i> (Å)	24.392(9)	11.373(2)	18.533(1)
α (°)	90	90	71.988(6)
β (°)	94.99(4)	90.54(1)	88.919(6)
γ (°)	90	90	69.843(5)
$V(Å^3)$	3543(2)	3870.3(11)	2621.2(3)
Ζ	4	4	2
D_{calc} (Mg m ⁻³)	1.378	1.361	1.273
Absorption coefficient (mm^{-1})	0.609	4.533	0.383
F(000)	1528	1656	1048
Crystal size (mm)	$0.52\times0.45\times0.25$	$0.18 \times 0.13 \times 0.05$	$0.40 \times 0.24 \times 0.08$
θ (°)	1.68-25.98	3.63-66.92	2.75-26.37
Limiting indices	$13 \leqslant h \leqslant 4$,	$-28\leqslant h\leqslant 28$,	$-12 \leqslant h \leqslant 15$,
	$-15 \leqslant k \leqslant 0$,	$-16 \leqslant k \leqslant 3$,	$-14 \leqslant k \leqslant 15$,
	$-30 \leqslant l \leqslant 30$	$0 \leq l \leq 13$	$22 \leqslant l \leqslant 23$
Reflections collected	9603	4420	18668
Independent reflections (R_{int})	6913 (0.0540)	3444 (0.0582)	10544 (0.0264)
Completeness to θ	25.98 99.8%	66.92 100.0%	26.37 98.5%
Absorption correction	none	psi-scan	semi-empirical from equivalents
Maximum and minimum transmission	0.8626 and 0.7404	0.7322 and 0.5025	0.9700 and 0.8619
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F ²
Data/restraints/parameters	6913/0/451	3444/1/252	10544/0/665
Goodness-of-fit (GOF) on F^2	1.040	0.991	1.063
Final R indices $(I > 2\sigma(I))$	$R_1 = 0.0677, wR_2 = 0.1787$	$R_1 = 0.0565, wR_2 = 0.1112$	$R_1 = 0.0644, wR_2 = 0.1251$
R indices (all data)	$R_1 = 0.1024, wR_2 = 0.2005$	$R_1 = 0.1744, wR_2 = 0.1412$	$R_1 = 0.1085, wR_2 = 0.1430$
Largest difference in peak and hole (e Å ⁻³)	1.110 and -1.502	0.272 and -0.320	0.533 and -0.353

Table 2

Selected bond distances (Å) and bond angles (°) for $[Co(HL^1-H)_2]Cl(1)$ and $[Co(HL^1-CH_3)_2]Cl(2)$.

$[Co(HL^{1}-H)_{2}]Cl(1)$			$[Co(HL^1-CH_3)_2]$	Cl (2)			
Co1-01	1.900(2)	N1-Co1-N7	99.88(11)	Co1-O1	1.909(3)	N1-Co1-O1	82.16(4)
Co1-N1	1.842(3)	02-Co1-N5	81.69(10)	Co1-N1	1.851(3)	N1-Co1-N3≠	100.80(16)
Co1-N3	1.919(3)	N5-Co1-N7	82.03(11)	Co1-N3	1.927(4)	N1≠- Co1-O1	95.50(14)
Co1-O2	1.896(2)	N1-Co1-O2	96.47(10)	Co1-O1≠	1.909(3)	N1-Co1-N3	81.58(16)
Co1-N5	1.839(3)	01-Co1-N3	163.65(10)	Co1−N1≠	1.851(3)	N1-Co1-N1	178.83(12)
Co1-N7	1.907(3)	02-Co1-N7	163.61(10)	Co1−N3≠	1.927(4)	01≠-Co1-N3≠	163.68(13)
		N1-Co1-N5	176.71(12)			01-Co-N3	163.68(13)
C3 - O1	1.296(4)	01-C3-N2	123.1(3)	C1-01	1.292(4)	01-C1-N2	124.2(4)
C3-N2	1.331(4)	C1-N1-N2	123.6(3)	C1-N2	1.342(5)	C1-N2-N1	106.6(3)
N2-N1	1.367(4)	C2-C1-N1	111.4(3	N1-N2	1.363(5)	C8-N1-N2	124.2(3)
C1-N1	1.294(4)	C1-C2-N3	113.1(3)	C8-N1	1.295(5)	N1-C8-C9	112.2(4)
C2-N3	1.302(4)	C2-N3-N4	118.9(3)	C9-N3	1.299(5)	N3-C9-C8	113.0(4)
N3-N4	1.398(4)	N3-N4-C28	117.7(3)	N3-N4	1.413(5)	C9-N3-N4	118.8(4)
C28-N4	1.367(4)	N4-C28-O4	121.2(3)	C10-N4	1.356(6)	C10-N4-N3	117.9(4)
C28-04	1.214(4)			C10-O2	1.219(6)	O2-C10-N4	121.7(5)
C21-O2	1.285(3)	02-C21-N6	123.8(3)				
C21-N6	1.334(4)	N6-N5-C19	123.5(3)				
N5-N6	1.362(4)	N5-C19-C20	111.6(3)				
C19-N5	1.304(4)	C19-C20-N7	113.0(3)				
C20-N7	1.306(4)	C20-N7-N8	118.9(3)				
N7-N8	1.402(4)	N7-N8-C10	119.8(3)				
C10-N8	1.329(5)	N8-C10 O3	122.0(4)				
C10-O3	1.218(5)						

 \neq (1 – x, y, –z + 1/2), Symmetry transformation used to generate equivalent atoms.

The stoichiometry together with the IR and UV–visible spectral data of the isolated neutral octahedral Co(III) complexes reveal that only one aroylhydrazone residue of each of the two bisaroylhydrazone ligands is coordinated to the central Co(III) via two diimine nitrogens and a deprotonated enolimine oxygen atom. The other two aroylhydrazone residues remain uncoordinated, where one

of the aroylhydrazones exists in the deprotonated enolimine form (Scheme 2-iii), while the other remains protonated (Scheme 2-ii). This is evident from the absence of both v(N-H) and v(C=O) stretching vibrations from their IR spectra. In the cationic octahedral Co(III) complexes, both of the two coordinated aroylhydrazone residues are in the deprotonated enolimine form, similar to that

Table 3	
Selected bond lengths (\mathring{A}) and bond angles (\circ) for $[Co(HI^2-CH_0)(I^2-CH_0)]$ (7)	

	8	()	() [
	Co1-O2	1.927(2)	02-Co1-N3	81.92(10)
	Co1-N3	1.851(2)	N1-Co1-N5	100.15(11)
	Co1-N5	1.925(3)	02-Co1-N1	95.72(10)
	Co1-O1	1.904(2)	N3-Co1-N5	82.12(11)
	Co1-N1	1.853(3)	02-Co1-N5	164.00(10)
	Co1-N7	1.917(3)	N3-C01-N1	175.53(12)
			01-Co1-N7	164.46(10)
	C5-01	1.289(4)	01-C5-N2	123.9(9)
	C5-N2	1.338(5)	C5-N2-N1	107.2(3)
	N2-N1	1.364(3)	N2-N1-C1	124.8(3)
	N1-C1	1.305(5)	N1-C1-C2	111.3(3)
	C2-N7	1.310(5)	C1-C2-N7	113.8(3)
	N7-N8	1.390(3)	C2-N7-N8	122.0(3)
	N8-C29	1.302(5)	N7-N8-C29	114.8(3)
	C29-04	1.287(4)		
	02-C13	1.296(4)	02-C13-N4	124.4(3)
	C13-N4	1.325(5)	C13-N4-N3	107.4(3)
	N4-N3	1.369(3)	N4-N3-C3	124.0(3)
	N3-C3	1.297(5)	N3-C3-C4	111.6(3)
	C4-N5	1.311(5)	C3-C4-N5	114.1(3)
	N5-N6	1.388(4)	C4-N5-N6	119.6(3)
	N6-C21	1.302(5)	N5-N6-C21	115.3(3)
	C21-O3	1.296(4)		
	O3-H30	1.16(3)	C21-O3-H30	122.44(3)
	O4-H30	1.30(3)	03-H30-O4	167.64(3)
			H30-O4-C29	122.45(3)
-				

proposed for the neutral complexes. The uncoordinated aroylhydrazone residue remains in the neutral ketoamide form (Scheme 2-i).

The ¹H NMR spectra of the cationic complexes (**1** and **2**) derived from diacetyl bis-aroylhydrazone) display two magnetically nonequivalent methyl singlets at *ca.* 2.63 and 2.67 ppm, in addition to a series of multiplets due to the hydrazide aromatic protons. The spectra also show a sharp singlet at 11.90 ppm, attributed to the N–H proton of the uncoordinated ketoamide residue. The ¹H NMR spectra of the neutral complexes (**3–6**) exhibit almost the same spectral pattern. However, the broad singlet at *ca.* 11.88 ppm, which disappears on deuteration, can be attributed to the hydrogen bonded OH proton of the uncoordinated enolimine residue. The spectra of the neutral complexes (**7** and **8**) are dominated by a series of aromatic multiplets due to the two phenyl rings of the diimine moiety and the hydrazide aromatic protons. The spectra also show the characteristic broad OH singlet of the uncoordinated enolimine residue.

The (+) ESI mass spectra of both the cationic $[Co(HL^1-R)_2]Cl(1$ and **2**) and neutral $[Co(HL^1-R)(L^1-R)]$ (**3**–**6**) complexes are more or less similar and display peaks corresponding to the molecular ion $[Co(HL^1-R)_2]^{1+}$. The spectra also show the monoligand $[Co(L^1-R)]^{1+}$ cation which is generated from the molecular ion by the expulsion of one of the bisaroylhydrazone ligands. Solvation of $[Co(L^1-R)]^{1+}$ resulted in the formation of $[Co(L^1-R)(DMF)]^{1+}$ and $[Co(L^1-R)(DMF)_2]^{1+}$ cations. Recombination of $[Co(L^1-R)]^{1+}$ with $[Co(HL^1-R)_2]^{1+}$ followed by solvation gave rise to the cationic



Fig. 1. Molecular structure of [Co(HL¹-H)₂]Cl (1).

cluster $[Co_2(L^1-R)_3(DMF)_2(CH_3OH)_2 + 2H]^{+2}$. The spectra are also characterized by the presence of the dimeric Co(II) species $[\{Co(L^1-R)\}_2 + H]^{1+}$, originating from the reduction of $[Co(L^1-R)]^{1+}$ followed by dimerization. The (+) ESI mass spectra of the neutral $[Co(HL^2-R)(L^2-R)]$ complexes (7 and 8) show similar spectral patterns as recorded for **3–6**.

3.2. X-ray molecular structures and self-assembly of complexes 1 and 2

The X-ray crystal structures of both [Co(HL¹–H)₂]Cl (1), Fig. 1, and $[Co(HL^1-CH_3)_2]Cl$ (2), Fig. 2, consist of the bisligand cationic molecular unit $[Co(HL^1-R)_2]^{1+}$ (R = H or CH₃) and chloride Cl⁻ as a counter ion. Different from Ni(II) and Cu(II) [3,10] complexes derived from diacetyl bisaroylhydrazone ligands, where the bisaroylhydrazone behaves as a dianionic N2O2 tetradentate ligand, each of $(HL^1-H)^{1-}$ and $(HL^1-CH_3)^{1-}$ in **1** and **2**, respectively, acts as a monoanionic N₂O tridentate ligand. The Co(III) centre in both **1** and **2** has a distorted octahedral geometry where the two bisarovlhydrazone ligands are bound to the Co(III) center via the two imine nitrogens and one deprotonated enolimine oxygen. forming two 5-membered chelate rings. The ketoamide oxygen in each ligand remains uncoordinated. Taking the standard uncertainties (su) into account, the bond distances between Co1 and the donor atoms N1, N3 and O1 of one ligand in 1, Table 2, (Co1-N1 = 1.842(3), Co-N3 = 1.919(3) and Co1-O1 = 1.900(2)Å) are more or less equal to those between Co1 and the donor atoms N5, N7 and O2 (Co-N5 = 1.839(3), Co1-N7 = 1.907(3) and Co1-O2 = 1.896(2)Å) of the other ligand. In **2**, however, the two bisaroylhydrazone ligands are equivalent and the bond distances between Co1 and the donor atoms N1, N3 and O1 (Co1-N1 = 1.851(3), Co1-N3 = 1.927(4) and Co1-O1 = 1.909(3)Å) are slightly longer than the corresponding bond distances recorded







Fig. 2. Molecular structure of [Co(HL¹-CH₃)₂]Cl (2).

for **1**. The mean C–O (*ca*. 1.291 Å), C–N (*ca*. 1.347 Å) and N–N (*ca*. 1.364 Å) bond distances of the coordinated aroylhydrazone residues in both **1** and **2**, Table 2, are in agreement with the deprotonated enolimine structure [2,3,8], while the corresponding mean bond distances (C–O (*ca*. 1.217 Å), C–N (*ca*. 1.351 Å) and N–N (*ca*. 1.393 Å) of the uncoordinated residue suggest the neutral ketoamide structure (Scheme 2-i) [2,3,20].

In the crystal lattice of **1**, each two adjacent cationic molecular units, $[Co(HL^{1}-H)_{2}]^{1+}$, are linked together through pairs of reciprocal hydrogen bonds (C17H17A···O2, C17···O2 = 3.472 Å) between the methyl H17A proton and the coordinated enolimine oxygen O2, forming a hydrogen bonded dimer. The dimeric structure is further stabilized by three pairs of reciprocal (CH··· π) interactions, namely (CH17A··· π_1 , CH17A···Cg1 = 3.072 Å), (CH18B··· π_2 , CH18B···Cg2 = 3.333 Å) and (CH17B··· π_3 , CH17B···Cg3 = 3.588 Å) where π_1 , π_2 and π_3 are the delocalized π systems of the five-membered chelate ring (Co1,O1,C3,N3, N1) as well as (C4–C9) and (C22–C27) phenyl rings of the coordinated benzoylhydrazone residues,

Table 4

Non-covalent bond interactions in $[Co(L^1-H)_2]Cl(1)$.

$D{-}H{\cdots}A$	D-H	$H{\cdots}A$	D···A	<d−h···a< th=""></d−h···a<>	
(i) Non-covalent bond interactions involved in dimer formation					
C17H17A · · · O2	0.960	2.659	3.472(6)	142.72	
C17H17A···Cg1	0.960	3.072	3.980	158.40	
C18H18BCg2	0.960	3.333	3.860	117.13	
C17H17B· · ·Cg3	0.959	3.588	4.304	133.46	
(ii) Non-covalent bo	nd interaction	s involved in	the chain of dime	ers	
C24H2403	0.931	2.454	3.281(7)	148.11	
C17H17C···C35	0.960	2.841	3.377	116.21	
(iii) Non-covalent bond interactions between dimer chains					
C18H18A ··· Cg4	0.961	3.425	3.817	106.92	
(iv) Non-covalent bond interactions between 2D layers					
C33H3303	0.930	2.661	3.520(6)	154.03	
(v) non-covalent bond interactions involving the Cl1 counter ion					
N4H4···Cl1	0.860	2.349	3.114(3)	148.32	
N8H8···Cl1	0.859	2.446	3.149(3)	139.41	
C18H18A···Cl1	0.961	2.928	3.728	141.47	
C36H36ACl1	0.959	2.841	3.636	140.87	
C36H36C···Cl1	0.960	2.908	3.797	154.43	

Cg1 = five-membered chelate ring (Co1, N1, N2, C3, O1) centroid.

Cg2 = phenyl ring (C4–C9) centroid.

Cg3 = phenyl ring (C22–C27) centroid.

Cg4 = phenyl ring (C11–C16) centroid.

and Cg1, Cg2 and Cg3 are respectively the corresponding centroids. The structure parameters of these CH $\cdots\pi$ interactions, Table 4, are within the range reported for this type of non-covalent bond interactions [21,22]. The dimers are assembled together via pairs of reciprocal hydrogen bonds (C24H24···O3, C24···O3 = 3.281 Å) as well as reciprocal pairs of interactions (C17H17C···C35, C17···C35 = 3.377 Å), giving rise to a chain of dimers extended along the *a* axis. The chains of dimers are connected together via pairs of interactions (C18H18A··· π_4 , CH18A···Cg4 = 3.425 Å) as well as pairs of reciprocal short contacts, between aromatic H31 and methyl H36B (H31····H36B = 2.151 Å), thus generating a two-dimensional layer extended parallel to the *ab* plane. The layers are further interconnected through hydrogen bonds (C33H33...O3) (C33...O3 = 3.520 Å) [23] to form a three-dimensional framework. The two Cl1 counter anions are enclosed in the cavity between the dimeric units and each Cl1 anion is involved in hydrogen bond formation with the two hydrazinic protons N4H and N8H (N4H···Cl1, N4···Cl1 = 3.114 Å; N8H···Cl1, N8···Cl1 = 3.149 Å) as well as the two methyl protons H18A and H36A (CH18A...Cl1, C18...Cl1 = 3.729 Å; CH36A...Cl1, C36...Cl1 = 3.636 Å) of one molecular unit and with an adjacent molecular unit (CH36C···Cl1, C36· · ·Cl1 = 3.797 Å).

In 2, two cationic molecular units are linked together by pairs of reciprocal hydrogen bonds (CH4 \cdots O2, C4 \cdots O2 = 3.508 Å) [23] between the uncoordinated ketoamide O2 oxygen atom and the CH4 proton of the aromatic ring in the coordinated p-methylbenzoylhydrazone residue, forming a hydrogen bonded dimer. The dimers are linked to each other through two pairs of additional hydrogen bonds (CH4 \cdots O2, C4 \cdots O2 = 3.508 Å), forming a chain of dimers propagating along the *c* axis. The chain is further stabilized by pairs of reciprocal interactions (C18H18A···C18, C18···C18 = 3.308 Å). The self-assembly of the cationic molecular units $[Co(HL^1-CH_3)_2]^{1+}$ resulted in the formation of a one-dimensional tubular structure extending along the *c* axis. The Cl1 counter anion is involved in a bifurcated hydrogen bond with the two N4H protons of the two uncoordinated ketoamide residues in each molecular unit (N4H···Cl1, N4···Cl1 = 3.184 Å). The two hydrogen bonds $(N4H \cdots Cl1)$ generate an 8-membered ring of graph set $R_2^1(8)$ [25]. The structural parameters of the non-covalent bonding interactions for complex 2 are listed in Table 5.

3.3. X-ray molecular structure and self-assembly of $[Co(HL^2-CH_3)(L^2-CH_3)]$ (7)

The X-ray crystal structure of **7**, Fig. 3, reveals that the Co(III) centre is in a distorted octahedral environment where the two bisaroylhydrazone ligands are meridionally coordinated around the Co(III) centre. One of the bisaroylhydrazone ligands acts as a mononegative N₂O tridentate anion and is coordinated to Co(III) via the two imine nitrogens (N3 and N5) (Co1–N3 = 1.851(2), Co1–N5 = 1.925(3) Å) and deprotonated enolimine oxygen O2 (Co1–O2 = 1.927(2) Å). The protonated enolimine oxygen O3 (O3–H = 1.166(3) Å) of the same ligand remains uncoordinated. The other bisaroylhydrazone acts as a dinegative N₂O tridentate ligand and is

 Table 5

 Non-covalent bond interactions in [Co(HDabh-CH₃)₂]Cl (2).

D−H···A	D-H	$H{\cdots}A$	$D{\cdots}A$	<d−h···a< td=""></d−h···a<>		
Intermolecular non-covalent bond interactions						
C4H4···O2	0.930	2.663(4)	3.508(4)	151.4		
C18H18AC18	0.959	2.813	3.308	113.1		
Intramolecular non-covalent bond interaction						
N4H4···Cl1	0.89(3)	2.34 (4)	3.164(4)	155.0(40)		



Fig. 3. Molecular structure of $[Co(HL^2-CH_3)(L^2-CH_3)]$ (7).

bound to the Co(III) centre through the two diimine nitrogens (N1 and N7)(Co1–N1 = 1.853(3), Co1–N7 = 1.917(3) Å) and the deprotonated enolimine oxygen O1 (Co1–O1 = 1.904(2) Å). The other deprotonated enolimine oxygen O4 remains uncoordinated, but is involved in a strong intramolecular hydrogen bond (O3–H···O4) with the uncoordinated enolimine proton of the other ligand. Formation of such a chelated proton [24] gives rise to an R_2^1 (10) macrocyclic ring [25]. The structural parameters of the intramolecular hydrogen bond (O3H···O4⁻), Table 6, suggest a strong interaction between the O3H enolimine proton and the negatively charged enolimine O4 oxygen and they are within the range expected for [HO···O⁻] hydrogen bonds [28].

Each molecular unit is linked to another neighboring molecular unit by a pair of reciprocal π - π stacking interactions [26,27] between the aromatic ring (C6–C11) of the coordinated aroylhydrazone residue and the benzil phenyl ring (C49–C54) of the adjacent molecular unit (Cg1–Cg2 = 3.981 Å), forming a π - π stacked dimer. The dimeric structure is stabilized by a pair of reciprocal H7…H19 (H7…H19 = 2.2906(1) Å) short contacts. The formed dimers are connected to each other by two pairs of reciprocal CH… π interactions [21] between the CH32 proton of the aroylhydrazone

Table 6

Non-covalent bond interactions in [Co(HL²-CH₃)(L²-CH₃)].

_	$D{-}H{\cdot}{\cdot}{\cdot}A$	D-H	H···A	D· · ·A	<d− H· · ·A</d−
Intramolecular non-covalent bond interactions					
	03-H3···04	1.167	1.297	2.448	167.64
	Intermolecular	non-covalent bond i	nteractions		
	π1-π2	Cg1-	C6-Cg1-Cg2 = 87.07		
		Cg2 = 3.981,			
			C9-Cg1-Cg2 = 92.88		
			C51-Cg2-		
			Cg1 = 79.30		
			C54-Cg3-		
			Cg1 = 98.20		
	C32H32…π1	0.930	3.220	4.093	157.02
	C58H58…π3	0.929	3.176	3.936	140.35
	$C38H38{\cdots}\pi2$	0.929	3.986	4.739	140.37

 π 1 = π – system of aromatic (C6–C11) ring (centeroid Cg1),

 $\pi 2 = \pi$ – system of aromatic (C49–C54) ring (centroid Cg2),

 π 3 = π – system of aromatic (C22–C27) ring (centroid Cg3).

aromatic ring (C30–C35) and the π -system of the other (C6–C11) ring (CH32…Cg1 = 3.220 Å) of the adjacent dimeric unit, giving rise to a linear chain of π – π stacked dimers propagating along the *b* axis. The chains are assembled together by pairs of reciprocal CH… π interactions between the CH58 proton of the benzil phenyl ring (C55–C60) and the π -system of the aroylhydrazone aromatic ring (C22–C27) (CH58…Cg3 = 2.876 Å), forming a two-dimensional layer of chains extended parallel to the *ac* plane. These ²D layers are further interconnected along the *a* axis through pairs of reciprocal interactions (CH38…Cg2, CH38…Cg2 = 3.986 Å), generating a three-dimensional framework.

4. Conclusions

In the present work, the octahedral cationic bisligand Co(III) complexes $[Co(HL^1-R)_2]Cl$ (R = H and CH₃) as well as octahedral neutral complexes $[Co(HL^1-R)(L^1-R)]$ (R = H, CH₃, OCH₃, Cl) and $[Co(HL^2-R)(L^2-R)]$ (H and CH₃) have been prepared and characterized. The X-ray crystal structures of $[Co(HL^1-R)_2]Cl(R = H and CH_3)$ reveal that the two bis(aroylhydrazone) ligands in each of these complexes are both coordinated to the Co(III) centre through the two diimine nitrogens and the deprotonated enolimine oxygen, while the keto amide oxygen remains uncoordinated (Scheme 2i). In the neutral Co(III) complexes $[Co(HL^1-R)(L^1-R)]$ (R = H, CH₃, OCH₃, Cl) and $[Co(HL^2-R)(L^2-R)]$ (H and CH₃), one of the two bisaroylhydrazones functions as a mononegative N₂O tridentate anion, while the other acts as a dinegative N₂O tridentate anion. Both the mono- and dinegative bisaroylhydrazone ligands are coordinated to the Co(III) centre via the two dimine nitrogens and the deprotonated enolimine oxygen. The uncoordinated residue of the mononegative ligand exists as a protonated enolimine oxygen (Scheme 2-ii), while the uncoordinated enolimine residue of the of the dinegative ligand is deprotonated (Scheme 2-iii). The X-ray crystal structure of $[Co(HL^2-CH_3)(L^2-CH_3)]$ shows that the free enolimine proton of the mononegative ligand is involved in a very strong hydrogen bond with the uncoordinated deprotonated enol imine oxygen of the dinegative ligand.

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Appendix A. Supplementary data

CCDC 929243, 929244 and 929276 contain the supplementary crystallographic data for $[Co(HL^1-CH_3)_2]Cl$, $[Co(HL^2-CH_3)(L^2-CH_3)]$ and $[Co(HL^1-H_3)_2]Cl$, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- L. El-Sayed, M.F. Iskander, N.M. Hawash, S.S. Massoud, Polyhedron 17 (1998) 199.
- [2] E. Lopéz-Torres, M.A. Mendiola, Dalton Trans. 37 (2009) 7639.
- [3] N.M.H. Salem, A.R. Rashad, L. El-Sayed, W. Haase, M.F. Iskander, Polyhedron 28 (2009) 2137.
- [4] L. Sacconi, G. Lombardo, P. Paoletti, J. Chem. Soc. (1958) 840.
- [5] L. Sacconi, G. Lombardo, R. Ciofalo, J. Am. Chem. Soc. 82 (1960) 4182.
- [6] L. Sacconi, G. Lombardo, P. Paoletti, J. Am. Chem. Soc. 82 (1960) 4185.
- [7] L. Sacconi, G. Lombardo, J. Am. Chem. Soc. 82 (1960) 6266.
- [8] H. Herack, B. Prelesnik, V.M. Leovac, S.Y. Chundak, Acta Crystallogr., Sect. C 47 (1991) 1408.
- [9] E. Lopéz-Torres, A.L. Medina-Castillo, J.F. Fermández-Sanchez, M.A. Mendiola, J. Organomet. Chem. 695 (21) (2010) 2305.
- [10] T. Ghosh, A. Mukhopadyay, S.C. Dargaiah, S. Pal, Struct. Chem. (2010) 147.

- [11] Orlandini, A. Dakterniks, L. Sacconi, Inorg. Chim. Acta 29 (1978) L205.
- [12] T. Ghosh, S. Pal, Inorg. Chim. Acta 363 (2010) 3632.
- [13] A. Bacchi, M. Carcelli, P. Pelagatti, C. Pelizzi, G. Pelizzi, C. Salati, P. Sgarabotto, Inorg. Chim. Acta 295 (1999) 171.
- [14] N.M.H. Salem, L. El Sayed, W. Haase, M.F. Iskander, J. Coord. Chem. 58 (2005) 1327.
- [15] Sheffield Chemputer Isotope Pattern; <www.shef.ac.uk/chemistry/ isotopes.Htm>.
- [16] G.M. Sheldrick, SHELXL-97, SHELEX-97: Program for Crystal Structure Analysis, University of Gottingen, Gottengen, Germany, 1998.
- [17] C.K. Johnson, M.N. Burnett, ORTEPIII, Report ORNL-6895, Oak Ridge National Laboratory, TN, USA, 1996.
- [18] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2002.

- [19] A.B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, Amsterdam, 1984.
- [20] S. Ianelli, M. Carcelli, J. Chem. Cryst. 31 (2001) 123.
 [21] M. Nishio, M. Hirota, Y. Umezawa, The CH/π interaction, Evidence, Nature and Consequences, Wiley, New York, 1998.
- [22] G.A. Bogdanovic, A. Spasojevic-de Bire, Eur. J. Inorg. Chem. (2002) 1599.
- [23] G.R. Desiraju, Acc. Chem. Res. 29 (1996) 441.
- [24] J.-C. Chambrone, M. Meyer, Chem. Soc. Rev. 38 (2009) 1663.
- [25] J. Bernstein, R.E. Davis, L. Shimoni, Angew. Chem. Int. Ed. Engl. 34 (1995) 1555.
- [26] C.A. Hunter, J.K.M. Sanders, J. Am. Chem. Soc. 122 (1990) 5525.
- [27] C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885.
- [28] G.A. Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press, New York, Oxford, 1997. Chapter 3.