

A family of polynuclear cobalt complexes upon employment of an indeno-quinoxaline based oxime ligand†

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The reaction of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with LH (LH = 11*H*-indeno[1,2-*b*]quinoxalin-11-one oxime) in MeOH in the presence of NEt_3 forms the complex $[\text{Co}^{\text{III}}_2\text{Co}^{\text{II}}\text{O}(\text{OAc})_3\text{L}_3] \cdot 0.5\text{MeOH} \cdot 0.2\text{H}_2\text{O}$ ($1 \cdot 0.5\text{MeOH} \cdot 0.2\text{H}_2\text{O}$), while repeating the reaction under solvothermal conditions yielded the heptanuclear cluster $[\text{Co}^{\text{II}}_7\text{L}_9(\text{OH})_2(\text{OAc})_{2.7}(\text{MeO})_{0.3}(\text{H}_2\text{O})] \cdot 4.6\text{MeOH} \cdot 3.3\text{H}_2\text{O}$ ($2 \cdot 4.6\text{MeOH} \cdot 3.3\text{H}_2\text{O}$). Changing the starting metal salt to $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and upon the reaction with LH in the presence of NEt_3 under high temperature and pressure, we managed to isolate the decanuclear cluster $[\text{Co}^{\text{II}}_{10}\text{L}_{14}(\text{OH})_{3.6}(\text{MeO})_{0.4}](\text{ClO}_4)_2 \cdot 8.5\text{MeOH} \cdot 5.75\text{H}_2\text{O}$ ($3 \cdot 8.5\text{MeOH} \cdot 5.75\text{H}_2\text{O}$), while under normal bench conditions and upon employment of pivalates in the reaction mixture complex $[\text{Co}^{\text{II}}_4\text{L}_4(\text{piv})_4(\text{MeOH})_2] \cdot \text{MeOH} \cdot \text{H}_2\text{O}$ ($4 \cdot \text{MeOH} \cdot \text{H}_2\text{O}$) was formed. Furthermore, the reaction of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with LH and aibH (2-amino-isobutyric acid) in the presence of NEt_3 in MeOH gave the mononuclear complex $[\text{Co}^{\text{II}}\text{L}(\text{aib})_2] \cdot 3\text{H}_2\text{O}$ ($5 \cdot 3\text{H}_2\text{O}$), while upon increasing the metal–ligand ratio cluster $[\text{Co}^{\text{III}}_2\text{Co}^{\text{II}}\text{L}_4(\text{aib})_2(\text{OH})_2] \cdot 7.9\text{MeOH}$ ($6 \cdot 7.9\text{MeOH}$) was isolated. Finally, repeating the reaction that yielded the mononuclear complex $5 \cdot 3\text{H}_2\text{O}$ under solvothermal conditions, gave the octanuclear cluster $[\text{Co}^{\text{II}}_8\text{L}_{10}(\text{aib})_2(\text{MeO})_2](\text{ClO}_4)_2 \cdot 6.8\text{MeOH} \cdot 7\text{H}_2\text{O}$ ($7 \cdot 6.8\text{MeOH} \cdot 7\text{H}_2\text{O}$). Variable temperature dc magnetic susceptibility studies for complexes 2, 3, 4 and 7, reveal that all clusters display dominant antiferromagnetic interactions leading to small or diamagnetic ground-states, S.

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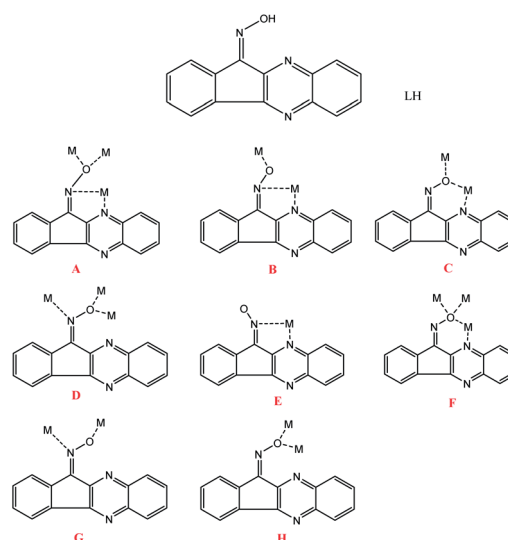
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Introduction

In the last few years metal-oxime coordination chemistry has proven to be a fruitful source for the synthesis and characterization of numerous metallic complexes.¹ Although initially triggered by the employment of salicyl- and pyridyl-based oximes in manganese cluster chemistry,² it later expanded to other 3d, 4f and 3d–4f clusters as well, while a palette of various oxime-based ligands is nowadays utilized for the synthesis of such species.³ In addition, many of these clusters have been found to display interesting magnetic properties, such as single molecule magnetism behaviour (SMM), *i.e.* they can retain their magnetization once magnetized at very low temperatures in the absence of an external magnetic field.

We recently reported the use of a new indeno-quinoxaline based oxime ligand, LH (Scheme 1), in Ni(II) chemistry, which

led to the synthesis of five nickel complexes with nuclearities ranging from 3 up to 8.⁴ We have now expanded our studies in Co(II/III) chemistry, and herein we report the use of this



Scheme 1 The structure of LH (top) and its coordination modes in 1–7 (bottom).

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indeno-quinoxaline oxime ligand for the synthesis of an extended family of cobalt complexes.

Experimental

Materials and physical measurements

All manipulations were performed under aerobic conditions using materials as received (reagent grade). **Caution!** Although we encountered no problems, care should be taken when using the potentially explosive perchlorate ions. LH was synthesized as described in the literature.⁵ Elemental analyses (C, H, N) were performed by the University of Ioannina microanalysis service. Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 5.0 K were collected on a Quantum Design MPMS-XL SQUID magnetometer (University of Crete) equipped with a 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants.

Syntheses

[Co₃O(OAc)₃L₃]·0.5MeOH·0.2H₂O (1·0.5MeOH·0.2H₂O). Co(OAc)₂·4H₂O (124 mg, 0.5 mmol), LH (124 mg, 0.5 mmol) and NEt₃ (2.0 mmol) were added in MeOH (20 ml) and the resulting mixture was stirred for 45'. The solution was filtrated and allowed to evaporate in room temperature. After 2 days, pink crystals of [Co₃O(OAc)₃L₃]·0.5MeOH·0.2H₂O were obtained in ~40% yield and collected by filtration, washed with Et₂O and dried in air. The complex analysed as solvent-free. Anal. calcd for C₅₁H₃₃N₉Co₃O₁₀: C, 55.25; H, 3.00; N, 11.37. Found: C, 55.39; H, 3.27; N, 11.23%.

[Co₇L₉(OH)₂(OAc)_{2.7}(MeO)_{0.3}(H₂O)]·4.6MeOH·3.3H₂O (2·4.6MeOH·3.3H₂O). Co(OAc)₂·4H₂O (124 mg, 0.5 mmol), LH (124 mg, 0.5 mmol) and NEt₃ (2.0 mmol) were added in MeOH (10 ml) and the resulting mixture was transferred to a Teflon-lined autoclave and kept at 120 °C for 12 hours. After slow cooling to room temperature, pink crystals of [Co₇L₉(OH)₂(OAc)_{2.7}(MeO)_{0.3}(H₂O)]·4.6MeOH·3.3H₂O were obtained in ~35% yield and collected by filtration, washed with Et₂O and dried in air. The complex analysed as 2·MeOH·H₂O. Anal. calcd for C_{141.7}H₉₁N₂₇Co₇O_{19.7}: C, 58.70; H, 3.16; N, 13.04. Found: C, 58.79; H, 3.41; N, 12.86%.

[Co₁₀L₁₄(OH)_{3.6}(MeO)_{0.4}](ClO₄)₂·8.5MeOH·5.75H₂O (3·8.5MeOH·5.75H₂O). Co(ClO₄)₂·6H₂O (183 mg, 0.5 mmol), LH (124 mg, 0.5 mmol) and NEt₃ (2.0 mmol) were added in MeOH (10 ml) and the resulting mixture was transferred to a Teflon-lined autoclave and kept at 120 °C for 12 hours. After slow cooling to room temperature, pink-red crystals of [Co₁₀L₁₄(OH)_{3.6}(MeO)_{0.4}](ClO₄)₂·8.5MeOH·5.75H₂O were obtained in ~25% yield and collected by filtration, washed with Et₂O and dried in air. The complex analysed as 3·MeOH·2H₂O. Anal. calcd for C_{211.4}H_{124.8}N₄₂Co₁₀O₂₉Cl₂: C, 58.00; H, 2.87; N, 13.44. Found: C, 58.20; H, 3.13; N, 13.27%.

[Co₄L₄(piv)₄(MeOH)₂]·MeOH·H₂O (4·MeOH·H₂O). The same procedure as that followed for complex 3·8.5MeOH·5.75H₂O was employed, with the addition of Napiv (0.062 mg, 0.5 mmol) in the reaction mixture. Pink crystals of [Co₄L₄(piv)₄(MeOH)₂]·MeOH·H₂O were formed after 3 days in ~35% yield. The

complex analysed as solvent-free. Anal. calcd for C₈₂H₇₆N₁₂Co₄O₁₄: C, 58.30; H, 4.53; N, 9.95. Found: C, 58.17; H, 4.79; N, 10.05%.

[CoL(aib)₂]·3H₂O (5·3H₂O). Co(ClO₄)₂·6H₂O (183 mg, 0.5 mmol), LH (124 mg, 0.5 mmol), aibH (52 mg, 0.5 mmol) and NEt₃ (2.0 mmol) were added in MeOH (20 ml) and the resulting mixture was kept under stirring for 45'. The solution was then filtrated and allowed to evaporate in room temperature. After 1 day, dark pink crystals of [CoL(aib)₂]·3H₂O were obtained in ~50% yield and collected by filtration, washed with Et₂O and dried in air. The complex analysed as 5·H₂O. Anal. calcd for C₂₃H₂₆N₅CoO₆: C, 52.38; H, 4.97; N, 13.28. Found: C, 52.27; H, 5.22; N, 13.47%.

[Co₃L₄(aib)₂(OH)₂]·7.9MeOH (6·7.9MeOH). The same procedure as that followed for complex 5·3H₂O was employed, with the addition of excess of Co(ClO₄)₂·6H₂O (732 mg, 2.0 mmol) in the reaction mixture. After 3 days, pink crystals of [Co₃L₄(aib)₂(OH)₂]·7.9MeOH were obtained in ~40% yield and collected by filtration, washed with Et₂O and dried in air. The complex analysed as 7·2MeOH. Anal. calcd for C₇₀H₅₈N₁₄Co₃O₁₂: C, 57.42; H, 3.99; N, 13.39. Found: C, 57.55; H, 4.27; N, 13.25%.

[Co₈L₁₀(aib)₂(MeO)₂](ClO₄)₂·6.8MeOH·7H₂O (7·6.8MeOH·7H₂O) and [Co₈L₁₀(aib)₂(MeO)₂](ClO₄)₂·MeOH·3H₂O (7·MeOH·3H₂O). Co(ClO₄)₂·6H₂O (183 mg, 0.5 mmol), LH (124 mg, 0.5 mmol), aibH (52 mg, 0.5 mmol) and NEt₃ (2.0 mmol) were added in MeOH (10 ml) and the resulting mixture was transferred to a Teflon-lined autoclave and kept at 120 °C for 12 hours. After slow cooling to room temperature, two kinds of crystals, dark brown 7·6.8MeOH·7H₂O and pale brown 7·MeOH·3H₂O, were obtained in ~35% yield and collected by filtration, washed with Et₂O and dried in air. The complex analysed as 7·MeOH·3H₂O. Anal. calcd for C₁₆₀H₁₀₈N₃₂Co₈O₂₇Cl₂: C, 55.65; H, 3.15; N, 12.98. Found: C, 55.79; H, 3.36; N, 12.85%.

X-ray crystallography

Diffraction data for complexes **1**, **3**, **4** and **6** at low temperatures were collected on an Xcalibur R diffractometer with CCD Ruby and for **2**, **5** and **7** on a KM4 diffractometer with a CCD Sapphire camera and Mo K α radiation ($\lambda = 0.71073$ Å). The crystal for **3** was slowly cooled from 230 K to 80 K, at which data collection was carried out. All structures were solved by direct methods and refined by full-matrix least-squares techniques on F² (SHELXL-97).⁶ Data collection parameters and structure solution and refinement details are listed in Table S1.†

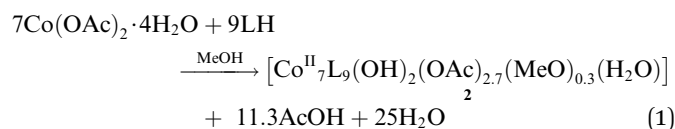
Results and discussion

Syntheses

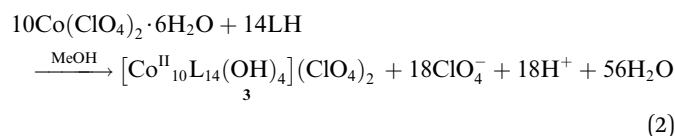
The reaction between Co(OAc)₂·4H₂O and LH in the presence of base (NEt₃) in MeOH yields the trinuclear cluster [Co^{III}₂Co^{II}O(OAc)₃L₃]·0.5MeOH·0.2H₂O (1·0.5MeOH·0.2H₂O) in moderate yield. Given the employment of excess base in the reaction, it is reasonable that all of the LH ligands found in **1** were in their deprotonated monoanionic form, L[−]. Furthermore, the acetates present in the reaction can also act as a base,



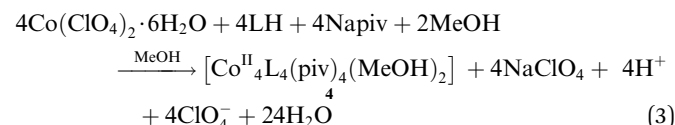
thus aiding the deprotonation of the ligand. Two of the three metallic centers were oxidized in the +3 oxidation state, presumably upon oxidation from the atmospheric dioxygen, a commonly observed phenomenon in cobalt chemistry. In order to investigate the effect of high pressure/temperature on the identity of the product, we repeated the same reaction under solvothermal conditions, and we obtained the heptanuclear cluster $[\text{Co}^{\text{II}}_7\text{L}_9(\text{OH})_2(\text{OAc})_{2.7}(\text{MeO})_{0.3}(\text{H}_2\text{O})] \cdot 4.6\text{MeOH} \cdot 3.6\text{H}_2\text{O}$ ($2 \cdot 4.6\text{MeOH} \cdot 3.6\text{H}_2\text{O}$) according to eqn (1), proving the effect of the solvothermal conditions on increasing the nuclearity of the product:



Furthermore, the oxidation of the metallic centers is now suppressed, since in the trinuclear cluster the ratio of $\text{Co}^{\text{III}} : \text{Co}^{\text{II}}$ was 2 : 1, while in the heptanuclear cluster all cobalt centers are maintained in the 2+ oxidation state, due to the “reducing” environment present within the autoclaves under high temperature/pressure.⁷ Upon removal of the carboxylates from the reaction mixture, and changing $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ to $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ we managed to isolate the decanuclear cluster $[\text{Co}^{\text{II}}_{10}\text{L}_{14}(\text{OH})_{3.6}(\text{MeO})_{0.4}] \cdot (\text{ClO}_4)_2 \cdot 8.5\text{MeOH} \cdot 5.75\text{H}_2\text{O}$ ($3 \cdot 8.5\text{MeOH} \cdot 5.75\text{H}_2\text{O}$) according to eqn (2):

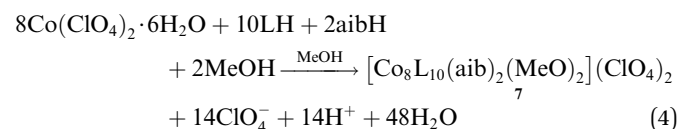


While the reaction forming **3** under normal laboratory conditions did not lead to the formation of any crystalline product, upon addition of pivalates in the reaction mixture we were able to isolate the tetranuclear cluster $[\text{Co}^{\text{II}}_4\text{L}_4(\text{piv})_4(\text{MeOH})_2] \cdot \text{MeOH} \cdot \text{H}_2\text{O}$ ($4 \cdot \text{MeOH} \cdot \text{H}_2\text{O}$), according to eqn (3):

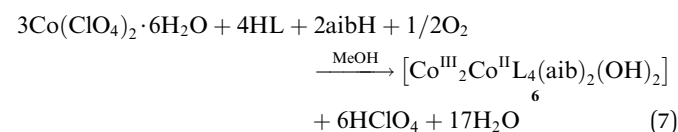
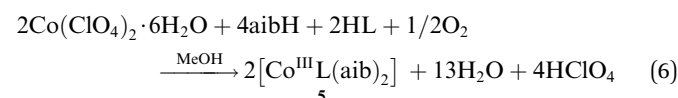
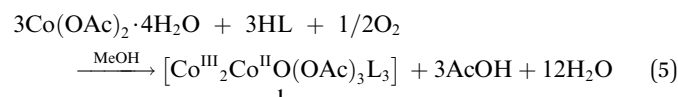


With the identity of cluster **4** established, we checked whether addition of other carboxylates would lead to analogous tetranuclear clusters. Therefore, we employed the artificial amino acid 2-amino-isobutyric acid, aibH, and we managed to characterize the mononuclear complex $[\text{Co}^{\text{III}}\text{L}(\text{aib})_2] \cdot 3\text{H}_2\text{O}$ ($5 \cdot 3\text{H}_2\text{O}$), whose identity was not surprising given the chelate coordination mode of the amino acid ligand (*vide infra*). In order to increase the nuclearity of the cluster, we increased the metal–ligands ratio as a means of “forcing” the cluster to propagate into bigger species due to the lack of sufficient number of chelates. Indeed, upon repeating the same reaction with twice the initial metal salt concentration, we isolated the trinuclear complex $[\text{Co}^{\text{III}}_2\text{Co}^{\text{II}}\text{L}_4(\text{aib})_2(\text{OH})_2] \cdot 7.9\text{MeOH}$ ($6 \cdot 7.9\text{MeOH}$) in moderate yields. Furthermore, repeating the reaction that yielded the mononuclear complex **5** $\cdot 3\text{H}_2\text{O}$ under

solvothermal conditions, gave the octanuclear cluster $[\text{Co}^{\text{II}}_8\text{L}_{10}(\text{aib})_2(\text{MeO})_2] (\text{ClO}_4)_2 \cdot 6.8\text{MeOH} \cdot 7\text{H}_2\text{O}$ ($7 \cdot 6.8\text{MeOH} \cdot 7\text{H}_2\text{O}$) according to eqn (4):



Finally, even though the formation of the complexes containing trivalent Co^{III} ions, clusters **1**, **5** and **6**, cannot be “strictly” given by chemical equations since we are not absolutely sure of the oxidizing-reduced species, their formation can be possibly described by the following eqn (5)–(7), assuming that the most likely oxidizing agent responsible for the $\text{Co}(\text{II})$ to $\text{Co}(\text{III})$ transformation is O_2 :



Description of structures

The molecular structures of complexes **1**–**7** are presented in Fig. 1–7, while selected interatomic distances and angles are listed in Tables S2–8.† Cluster **1** crystallizes in the trigonal $R\bar{3}$ space group. Its structure (Fig. 1) describes an oxo-centered equilateral triangular unit, which consists of three diatomic ($-\text{N}-\text{O}-$)_{oximate} bridges, from three deprotonated L^- ligands, and three $\eta^1:\eta^1:\mu$ acetate ligands. All L^- ligands adopt coordination mode B (Scheme 1), while each Co center is in a *cis*- O_4N_2 coordination sphere. The formula of the molecule necessitates a $[\text{Co}^{\text{III}}_2\text{Co}^{\text{II}}]$ oxidation states' distribution, but since the molecule lies on a special position (on a three-fold axis), and is disordered around it, we cannot assign the oxidation states of the metallic atoms. Similar examples of disordered mixed oxidation states have been previously reported in the literature.⁸

Complex **2** crystallizes in the triclinic $P\bar{1}$ space group. Its core (Fig. 2) describes an almost planar heptametalllic disc. The metallic disk is held together *via* nine deprotonated mono-anionic L^- ligands, three acetate and two methoxide ligands. The nine L^- ligands found in the structure, adopt four different coordination modes: (i) four are found in mode B (Scheme 1), forming a chelate ring *via* the oximate and one aromatic N atoms and bridging to a further Co center *via* the $\text{O}_{\text{oximate}}$ atom, (ii) two form a chelate ring *via* the oximate and one aromatic N atoms and bridging to two further Co centers *via* the $\mu\text{-O}_{\text{oximate}}$ atom (mode A), (iii) two are found in a rather unusual mode,



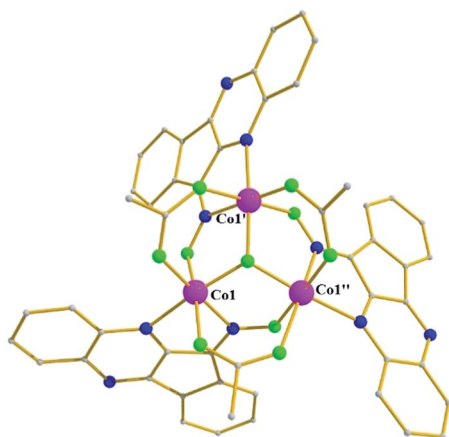


Fig. 1 Molecular structure of complex 1. Color code: Co = pink, O = green, N = blue, C = grey. Minor components of acetate and H atoms are omitted for clarity.

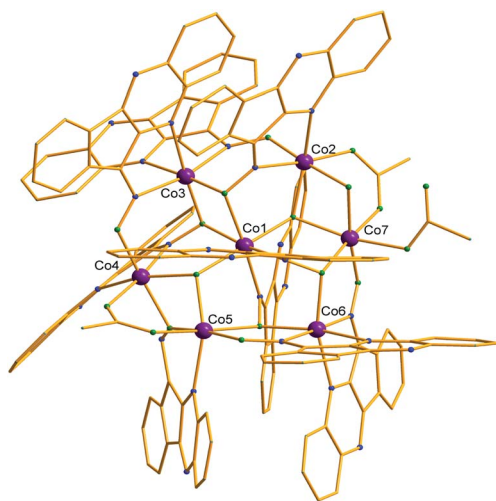


Fig. 2 Molecular structure of cluster 2. Color code: same as in Fig. 1. Disorder and H atoms as well as solvent molecules not shown for clarity.

bridging three metals *via* the monoatomic μ -O_{oximate} bridge and the N_{oximate} atom (mode D), and (iv) one in mode C (Scheme 1) *via* the O_{oximate} and N_{aromatic} atoms. Two acetate ligands adopt the usual $\eta^1 : \eta^1 : \mu$ mode, while the third one is found terminally bound. Finally, the two hydroxides are found in a μ_3 fashion, and in addition a H₂O molecule bridges Co2 and Co7 as a monoatomic bridge. All cobalt centers are found in the 2+ oxidation state, as evidenced by their bond distances, as well as BVS calculations (BVS values ranging from 1.76–2.03), and are found in an octahedral geometry adopting *cis*-O₄N₂ (Co1, Co2, Co4), *cis*-O₂N₄ (Co6, Co3), O₅N (Co5) and O₆ (Co7) coordination environment.

Cluster 3 also crystallizes in the triclinic $P\bar{1}$ space group; its metallic core consists of ten edge-sharing [Co₃] triangles, forming a slightly bent [Co₁₀] disc (Fig. 3) with dimensions of $\sim 10 \times 6$ Å. The ten metallic centers are held in position by fourteen monoanionic L[−] ligands which adopt six different

coordination modes: (i) five are found in mode B, (ii) three in mode F in which the O_{oximate} forms a six-member chelate ring with the N_{aromatic} and further bridges to two cobalt centers, (iii) two in mode D, (iv) one in mode G, (v) one in mode C, according to which the O_{oximate} forms a six-member ring with the N_{aromatic} and further bridges to one metallic center, and (vi) two in mode A. In addition, the coordination environment of the metallic centers is completed by the presence of three μ_3 -OH[−] and one μ -OH[−]. Co5, Co8 and Co7 are five-coordinate adopting distorted tetragonal pyramidal for the former two centers and highly distorted trigonal bipyramidal geometry for the remaining center, with τ values of 0.26, 0.30 and 0.62 respectively, while all remaining centers are six-coordinate adopting octahedral geometry.⁹ Furthermore, the coordination spheres of the metallic centers are O₆ (Co1), O₅N (Co2, Co9), *cis*-O₂N₄ (Co3, Co4, Co6) and *fac*-O₃N₃ (Co10) sphere. Finally, all metallic centers are in the 2+ oxidation state, as derived from BVS calculations yielding values in the 1.77–2.04 range.

Complex 4 (Fig. 4) crystallizes in the monoclinic space group *C2/c* in special position of *C*₂ symmetry; its metallic core describes a tetrahedron of four Co²⁺ ions linked together by (i) four fully deprotonated L[−] ligands in mode A, forming a distorted [Co₄(NO)₄]⁴⁺ cube comprising alternate single (O) and double (N–O) atom edges, and (ii) two $\eta^1 : \eta^1 : \mu$ pivalate ligands. Finally, two terminal pivalate ligands and two methanol molecules complete the coordination environment of the metal centers. The dimensions of the metallic tetrahedron are in the range 3.09–4.43 Å with the shortest distance between Co1 and Co2, and the longest between Co1 and Co1'. All metals are found in the 2+ oxidation state (BVS values: 2.16 for Co1 and 2.17 for Co2, Fig. 4), and are six-coordinate.

The mononuclear complex 5 crystallizes in the monoclinic *P2₁/c* space group. Its structure (Fig. 5) consists of a central Co³⁺ ion coordinated by one chelate L[−] ligand *via* its oximate and one

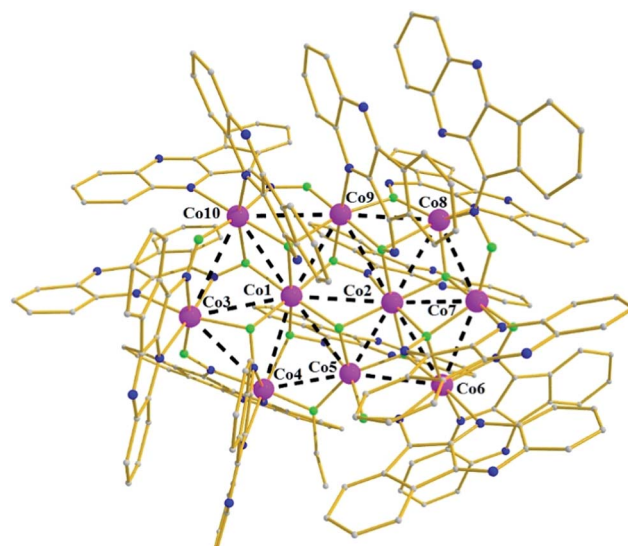


Fig. 3 Molecular structure of the cationic part of 3. Color code: same as in Fig. 1. Disorder and H atoms as well as solvent molecules not shown for clarity.



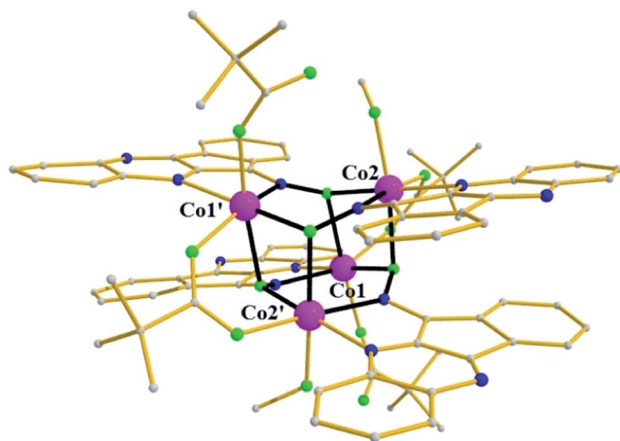


Fig. 4 The molecular structure of cluster 4, highlighting its cube-like core. Color code: same as in Fig. 1. Disorder and H atoms not shown for clarity. Symmetry code: ' = $-x + 1, y, -z + 1/2$.

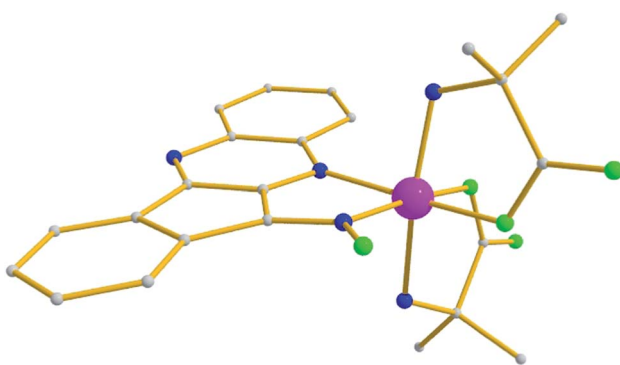


Fig. 5 Molecular structure of complex 5. Color code: same as in Fig. 1. Disorder and H atoms as well as solvent molecules not shown for clarity.

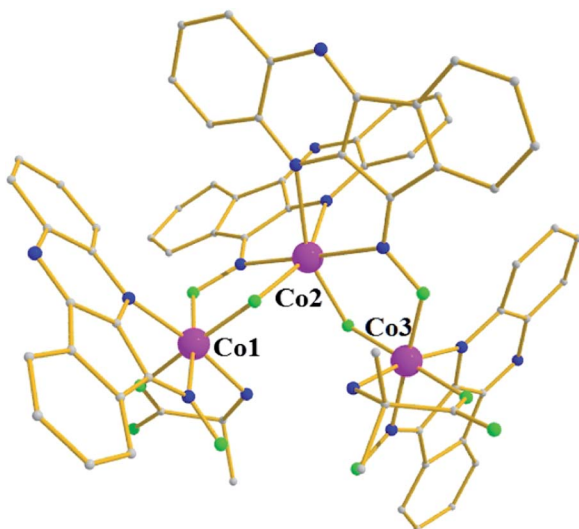


Fig. 6 Molecular structure of complex 6. Color code: same as in Fig. 1. Disorder and H atoms not shown for clarity.

aromatic N atoms (mode E), and two aib^- ligands in a chelate mode, thus forming three five-member chelate rings. The metal ion is found in a $\text{cis-O}_2\text{N}_4$ sphere, while BVS calculations yielded a value of 3.11 for the central metal atom.

Complex 6 crystallizes in the monoclinic space group $P2_1/n$. The structure consists of a trimetallic unit with a "V-shape" arrangement of the three metallic centers (Fig. 6), which are held together by two deprotonated ligands, L^- , found in mode B, and two $\mu\text{-OH}^-$ groups. Each terminal metallic atom is further coordinated to a deprotonated chelate L^- ligand (mode E) and to one chelate aib^- ligand. The formula of the complex necessitates a mixed-valent $\text{Co}^{\text{III}}_2\text{Co}^{\text{II}}$ oxidation state, and according to BVS calculations the two terminal cobalt atoms are in the 3+ oxidation state (BVS values of 3.15 and 3.22 for Co1 and Co3, respectively), while the central one in the 2+ (BVS value: 2.01). All metallic centers are six-coordinate adopting

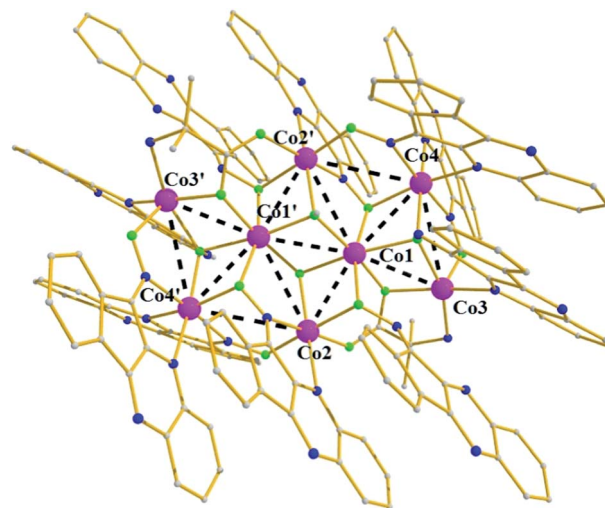


Fig. 7 Molecular structure of the cationic part of complex 7. Color code: same as in Fig. 1. H atoms and solvent molecules not shown for clarity. Symmetry code ' = $-x + 1, -y + 1, -z + 1$.

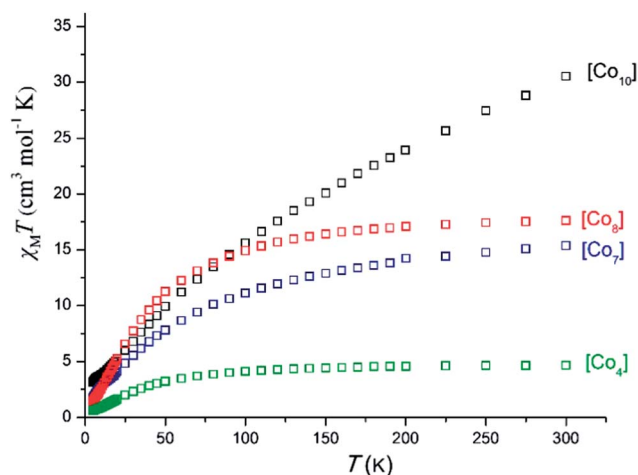


Fig. 8 Plot of $\chi_M T$ vs. T for complexes 2 ($[\text{Co}_7]$), 3 ($[\text{Co}_{10}]$), 4 ($[\text{Co}_4]$) and 7 ($[\text{Co}_9]$) under an applied dc field of 1000 G.



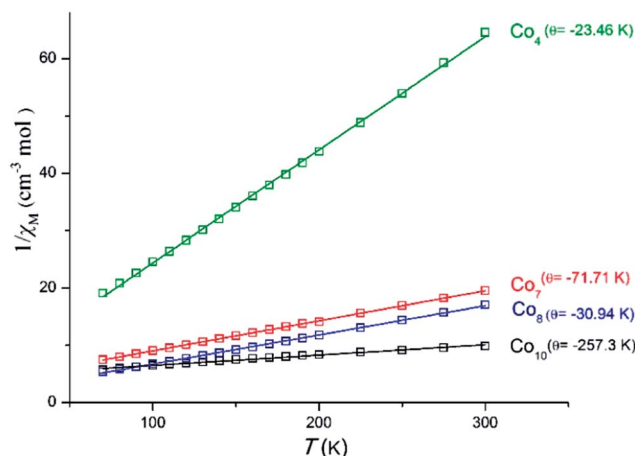


Fig. 9 Curie-Weiss plot for complexes 2, 3, 4 and 7 in the 50–300 K range.

octahedral geometry, with Co1 and Co3 in a *mer*-O₃N₃ coordination sphere, and Co2 in a *cis*-O₄N₂ arrangement.

Finally, complex 7 crystallizes in the triclinic $P\bar{1}$ space group in special position – center of symmetry. Its metallic core (Fig. 7) consists of a planar octametallic disk, in which the eight metallic centers are held in position by ten deprotonated, L[−],

ligands adopting four different coordination modes; (i) two in mode A, (ii) four in mode B, (iii) two in a monoatomic bridge fashion *via* the O_{oximate}, mode H, and (iv) two in mode F. In addition, two deprotonated aib[−] ligands are present in an $\eta^2 : \eta^1 : \eta^1 : \mu_3$ fashion, while two μ_3 -OCH₃[−] groups complete the coordination environment of the octametallic disc. All cobalt atoms are six-coordinate, besides Co3 (and its symmetry related Co3') which is five coordinate adopting tetragonal pyramidal ($\tau \approx 0$). Finally, all cobalt centers are in the 2+ oxidation state, as evidenced by BVS calculations giving values in the 1.75–2.01 range.

Magnetochemistry

Dc magnetic susceptibility studies. Direct current magnetic susceptibility studies were performed on polycrystalline samples of 2, 3, 4 and 7 in the 5–300 K range under an applied field of 0.1 T. The results are plotted as the $\chi_M T$ product *vs.* T in Fig. 8. Given the presence of octahedral Co^{II} ions with ⁴T_{1g} ground term, that splits to a doublet ground-state at low temperature when in distorted environment due to spin-orbit coupling,¹⁰ it is very laborious and extremely difficult to apply an exact theoretical model for fitting the magnetic susceptibility data.¹¹ Furthermore, Co(II) ions when in octahedral geometry may be treated as pseudo “ $S_{\text{eff}} = 1/2$ ” systems at low

Table 1 Structurally characterized heptanuclear cobalt [Co₇] clusters^a

Formula	Ox. states	S	θ (K)	Ref.
[Co ₇ (dea) ₆ (CH ₃ COO) ₃]	4Co ²⁺ , 3Co ³⁺	—	—	13
[Co ₇ (2poap-2H) ₅]	3Co ²⁺ , 4Co ³⁺	—	—	14
[Co ₇ (L ¹) ₁₂ Cl ₂]	7Co ²⁺	—	—	15
[Co ₇ (L ²) ₂ (OAc) ₄ O ₂ (DMF) ₂]	7Co ²⁺	—	—	16
[Co ₇ (bm) ₁₂]	7Co ²⁺	21/2	+1.16	17
[Co ₇ (HL ³) ₆ (NO ₃) ₃ (H ₂ O) ₃]	4Co ²⁺ , 3Co ³⁺	2	—	18
[Co ₇ O ₂ (O ₂ CCH ₃) ₈ (NCO) ₂ (HNPEt ₃) ₄]	7Co ²⁺	—	—	19
[Co ₇ (hdeo) ₆ (N ₃) ₆]	7Co ²⁺	7/2	+4.89	20
[Co ₇ (OH) ₆ (L ⁴) ₆]	6Co ²⁺ , 1Co ³⁺	—	—	21
[Co ₇ (OH) ₆ (L ⁵) ₆]	7Co ²⁺	7/2	+1.16	22
[Co ₇ (CH ₃ O) ₆ (L ⁵) ₆]	7Co ²⁺	7/2	+0.74	22
[Co ₇ (N ₃) ₆ (L ⁵) ₆]	7Co ²⁺	7/2	+1.88	22
[Co ₇ (L ⁶) ₁₂]	7Co ²⁺	—	−3.8	23
[Co ₇ (L ⁷) ₆ (MeO) ₆]	3Co ²⁺ , 4Co ³⁺	7/2	—	24
[Co ₇ (bhqe) ₃ (OH) ₂ (H ₂ O) ₆]	7Co ²⁺	7/2	+12	25
[Co ₇ (eimp) ₆ (OMe) ₆]	7Co ²⁺	—	−6.46	26
[Co ₇ O ₄ (O ₂ CCMe ₃) ₉ (HO ₂ CCMe ₃)(H ₂ O) ₃]	3Co ²⁺ , 4Co ³⁺	—	—	27
[Co ₇ (thme) ₂ (O ₂ CCMe ₃) ₈ Br ₂]	6Co ²⁺ , 1Co ³⁺	3	—	28
[Co ₇ (thme) ₂ (O ₂ CMe) ₁₀ (H ₂ O) ₄]	6Co ²⁺ , 1Co ³⁺	—	—	28
[Co ₇ S ₆ I ₃ (PEt ₃) ₄]	6Co ²⁺ , 1Co ³⁺	—	—	29
[Co ₇ (immp) ₆ (CH ₃ O) ₆]	7Co ²⁺	—	−1.39	30
[Co ₇ (bzip) ₆ (N ₃) ₉ (CH ₃ O) ₃]	7Co ²⁺	7/2	+37.3	31
[Co ₇ (OH) ₆ (L ⁸) ₆]	7Co ²⁺	—	—	32
[Co ₇ (MeOH) ₂ (OH) ₆ (L ⁸) ₆]	7Co ²⁺	—	—	32
[Co ₇ (L ⁹) ₆ (OH) ₆ (NO ₃) ₂]	6Co ²⁺ , 1Co ³⁺	—	—	32
[Co ₇ L ₉ (OH) ₃ (OAc) ₂ (H ₂ O)]	7Co ²⁺	—	−71.71	t.w

^a H₂dea = diethanolamine; poap: tritopic pyridine dihydrazone ligand; HL¹: pyridine-2-ylmethanol; H₃L²: tris[3,5-bis(methyl)-benzoic acid]-cyclo-tricethylene; Hbm = (1*H*-benzimidazol)-methanol; H₃L³ = H₂NC (CH₂OH)₃; Hhdeo = 2-hydroxy-[1,2-di (pyridin-2-yl)]ethane-1-one; (L⁴)[−] is the anion of 2-(pyridine-2-yl)pentane-2-ol-4-one; HL⁵: 2-methoxy-6-[(methylimino)-methyl]phenol; HL⁶: 6-methyl-2-pyridone; H₂L⁷: 1,1,1-trifluoro-7-hydroxy-4-methyl-5-aza-hept-3-en-2-one; H₄bhqe: 1,2-bis(8-hydroxyquinolin-2-yl)ethane-1,2-diol; Heimp: 2-ethoxy-6-(iminomethyl)-phenol; H₃thme: 1,1,1-tris(hydroxymethyl)ethane; Immp: 2-iminomethyl-6-methoxy-phenolic anion; bzip = 2-benzoyl pyridine; HL⁸ = 2-iminomethyl-6-methoxyphenol; HL⁹ = 2-iminophenyl-6-methoxyphenol.

Table 2 Structurally characterized octanuclear cobalt [Co₈] clusters^a

Formula	Ox. states	S	θ (K)	Ref.
[Co ₈ S ₆ (SPh) ₈]	4Co ²⁺ , 4Co ³⁺	—	—	33
[Co ₈ (NPh) ₉ (PPh ₃) ₂]	7Co ²⁺ , 1Co ³⁺	—	—	34
[Co ₈ S ₆ (SPh) ₈]	4Co ²⁺ , 4Co ³⁺	—	—	35
[Co ₈ (L ¹) ₄ (OH) ₂ (H ₂ O) ₄ (NO ₃) ₂ (bpy) ₄]	8Co ²⁺	—	—	36
[Co ₈ OQ ₁₂]	8Co ²⁺	—	−59	37
(PPh ₄)[Co ₈ S ₆ Br ₂ Cl ₂ (PPh ₃) ₄]	1Co ¹⁺ , 7Co ²⁺	—	—	38
[Co ₈ Piv ₈ (OH) ₆ (HPiv) ₄ (H ₂ O) ₂ (L ²) ₂]	8Co ²⁺	—	—	39
[Co ₈ (OMe) ₂ (L ³) ₄ (LH) ₂ (2-hp) ₄ (MeCN) ₄]	8Co ²⁺	4	+2.75	40
[Co ₈ O ₂ (O ₂ CN ¹ Pr ₂) ₁₂]	8Co ²⁺	—	—	41
[Co ₈ (MeCO ₂) ₈ (OMe) ₁₆]	8Co ³⁺	—	—	42
[Co ₈ O ₄ (CH ₃ CO ₂) ₆ (OMe) ₄]Cl ₄ (OH) ₂	2Co ²⁺ , 6Co ³⁺	—	—	43
[Co ₈ (chp) ₁₀ (O ₃ PPh) ₂ (NO ₃) ₃ (Hchp) ₂]	8Co ²⁺	—	—	44
[Co ₈ (IBT) ₁₂] ^{14−}	2Co ²⁺ , 6Co ³⁺	—	—	45
[Co ₈ (L ⁴) ₄ (OH) ₄ (MeOH) ₁₆]	8Co ²⁺	3/2	—	46
[Co ₈ Na ₂ (OH) ₂ (chp) ₂ (O ₂ CCPh) ₈ (HCO ₂) ₆ (Hchp) ₂ (EtOAc) ₂]	8Co ²⁺	—	—	47
[Co ₈ (TC4A) ₂ (N ₃) ₂ (N ₆ H ₂) ₂ (CH ₃ COO) ₄]	8Co ²⁺	—	−24.8	48
[Co ₈ (L ⁵) ₄ (H ₂ O) ₂ X] (X: H ₂ O or EtOH)	8Co ²⁺	0	−39	49
[Co ₈ O ₂ (L ⁶) ₆]	8Co ²⁺	—	—	50
[Co ₈ O ₂ (OCCMe ₃) ₁₂] (n: 2 or 3)	8Co ²⁺	—	—	51 and 52
[Co ^{II} ₈ L ₁₀ (aib) ₂ (MeO) ₂](ClO ₄) ₂	8Co ²⁺	—	−30.9	t.w.

^a H₂L¹: 1,3-bis-(3-oxo-3-(2-pyridyl)-propionyl)-pyridine; HQ: 8-hydroxyquinoline; L²: modified 2,4,4,5,5-pentamethyl-4,5-dihydro-1H-imidazole-(3-oxide)-1-oxyl; L³: 2,2'-biphenol, 2-hpH: 2-hydroxypyridine; Hchp: 6-chloro-2-hydroxypyridine; H₃IBT: 4,5-bis(tetrazol-5yl)imidazole; H₂L⁴: 2,6-bis-[5-(2-pyridinyl)-1H-pyrazole-3-yl] pyridine; chp = 6-chloro-2-pyridonate; H₄TC4A: *p*-tert-butylthiacalix[4]arene; H₄L⁵: 3-hydroxysalamo; L⁶: bis-bidentate ligand.

Table 3 Structurally characterized decanuclear cobalt [Co₁₀] clusters^a

Formula	Ox. st.	S	θ (K)	Ref.
[Co ₁₀ (Q) ₁₂ (CO ₃) ₄]	10Co ²⁺	—	−21.1	12
[Co ₁₀ (OH) ₆ (chp) ₆ (<i>o</i> -MeBz) ₇ (<i>n</i> -C ₃ H ₇ OH) ₅][<i>o</i> -MeBz]	10Co ²⁺	—	—	53
[Co ₁₀ (OH) ₆ (mhp) ₆ (<i>p</i> -tBuBz) ₈ (Hmhp) ₂ (CH ₃ CN) ₂]	10Co ²⁺	—	—	53
[Co ₁₀ (OH) ₆ (mhp) ₆ (O ₂ CPh) ₇ (Hmhp) ₃ Cl(MeCN)]	10Co ²⁺	—	—	54
[Co ₁₀ (OH) ₆ (mhp) ₆ (O ₂ CCMe ₃) ₇ Cl(MeCN) ₃ (Hmhp)]	10Co ²⁺	—	—	54
[Co ₁₀ (OH) ₄ (chp) ₁₀ (O ₂ CCMe ₃) ₆ (EtOH) ₂]	10Co ²⁺	—	—	54
[Co ₁₀ Piv ₁₄ (HPiv) ₂ L ² L ³] ₂]	10Co ²⁺	—	—	55
[Co ₁₀ O(dpm) ₄ (tmp) ₄ (AdCO ₂) ₂ (AdCO ₂ H) _{0.5} (MeOH) _{3.5} (H ₂ O) _{1.5}]	10Co ²⁺	—	—	12
[Co ₁₀ O(OH)(dpm) ₄ (cht) ₂ (Hcht) ₂ (AdCO ₂) ₃ (EtOH) ₃]	10Co ²⁺	—	—	12
[Co ₁₀ (OH) ₆ (mhp) ₆ (O ₂ CCPh) ₆ (Hmhp) ₃ (HCO ₃) ₃]	9Co ²⁺ , 1Co ³⁺	—	—	56
[Co ₁₀ (OH) ₂ (chp) ₁₄ (O ₃ PCH ₂ CH ₂ PO ₃) ₃]	10Co ²⁺	—	—	57
[Co(OH)(4-NO ₂ -pz)(3,5-Me ₂ -pz)] ₁₀	10Co ³⁺	—	—	58
[Co ₁₀ (chp) ₁₂ (O ₃ PPh) ₂ (O ₂ CPh) ₄ (H ₂ O) ₄]	10Co ²⁺	—	—	59
[Co ₁₀ (chp) ₁₂ (O ₃ PPh) ₂ (O ₂ C ^t Bu) ₄ (H ₂ O) ₄]	10Co ²⁺	—	—	59
[Co ₁₀ (chp) ₁₂ (O ₃ PPh) ₂ (O ₂ CPh ^t Bu) ₄ (H ₂ O) ₄]	10Co ²⁺	—	—	59
[Co ₁₀ (chp) ₁₂ (O ₃ PPh) ₂ (O ₂ CPh-2-Ph) ₄ (H ₂ O) ₄]	10Co ²⁺	—	—	59
[Co ₁₀ (chp) ₁₂ (O ₃ PMe) ₂ (O ₂ CPh-2-Ph) ₄ (H ₂ O) ₄]	10Co ²⁺	—	—	59
[Co ₁₀ (chp) ₆ (O ₃ PCH ₂ Ph) ₂ (O ₂ CPh) ₈ (F) ₂ (H ₂ O) ₂]	10Co ²⁺	—	—	59
[Co ₁₀ (chp) ₈ (O ₃ PCH ₂ Ph) ₂ (O ₂ CPh) ₈ (F) ₂ (MeCN) ₂]	10Co ²⁺	—	—	59
[Co ₁₀ (chp) ₆ (O ₃ PCH ₂ Ph) ₂ (O ₂ C ^t Bu) ₈ (F) ₂ (H ₂ O) ₂]	10Co ²⁺	—	—	59
[Co ₁₀ (chp) ₆ (O ₃ PMe) ₂ (O ₂ C ^t Bu) ₈ (F) ₂ (MeCN) ₄]	10Co ²⁺	—	—	59
[Co ₁₀ (chp) ₆ (O ₃ PEt) ₂ (O ₂ CPh) ₈ (F) ₂ (MeCN) ₄]	10Co ²⁺	—	—	59
[Co ₁₀ (chp) ₆ (O ₃ POct) ₂ (O ₂ CPh) ₈ (F) ₂ (MeCN) ₄]	10Co ²⁺	—	—	59
[Co ₁₀ (chp) ₈ (Hchp) ₂ (O ₃ PCH ₂ Nap)(O ₂ CPh) ₇ (OH) ₃]	10Co ²⁺	—	—	59
[Co ₁₀ L ₁₄ (OH) ₃ (MeO)](ClO ₄) ₂	10Co ²⁺	—	−257	t.w.

^a Q: 8-hydroxyquinoline, chp: 2-chloro-6-pyridonate, *o*-MeBz = 2-methylbenzoate, mhp: 2-methyl-6-pyridonate, Hmhp: 2-methyl-6-hydroxypyridine, *p*-tBuBz: 4-*tert*-butylbenzoate, Piv: (CH₃)₃CCO₂[−], L²L³: modified molecules of the starting NIT-Me (2,4,4,5,5-pentamethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl) and/or Im-Me (2,4,4,5,5-pentamethyl-4,5-dihydro-1H-imidazole-1-oxyl), Hdpm: dipivaloylmethane, H₃tmp: [1,1,1-tris(hydroxymethyl)propane, EtC(CH₂OH)₃], AdCO₂H: adamantyl carboxylic acid, H₃cht: *cis,cis*-1,3,5-cyclohexanetriol, mhp: 6-methyl-2-pyridonate, Hchp: 6-chloro-2-hydroxypyridine, O₂C^tBu: pivalate, O₂CPh^tBu: 4-*tert*-butylbenzoic acid, O₂CPh-2-Ph: 2-biphenylcarboxylic acid.



temperature due to the splitting of the Kramers doublets. Therefore, we feel it is prudent to attempt only a qualitative analysis of the data, in order to avoid misinterpretation of the magnetic data.

For complex 2 ($[\text{Co}_7]$) the room temperature $\chi_{\text{M}}T$ value of $15.39 \text{ cm}^3 \text{ K mol}^{-1}$ corresponds to seven non-interacting Co^{II} ions with $S = 3/2$ and $g = 2.17$. Upon cooling the $\chi_{\text{M}}T$ value decreases to reach a minimum value of $1.70 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K, suggesting the presence of dominant antiferromagnetic interactions. For cluster 4 ($[\text{Co}_4]$) the room temperature $\chi_{\text{M}}T$ value of $4.64 \text{ cm}^3 \text{ K mol}^{-1}$ is very close to the spin-only value of $4.411 \text{ cm}^3 \text{ K mol}^{-1}$ corresponding to two non-interacting Co^{II} ions. Upon cooling, this value remains constant until $\sim 90 \text{ K}$, before it decreases to reach the minimum value of $0.62 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K, with this behavior suggesting the presence of dominant, albeit weak, antiferromagnetic interactions. A similar behavior is encountered for cluster 7 ($[\text{Co}_8]$); the room temperature $\chi_{\text{M}}T$ value of $17.61 \text{ cm}^3 \text{ K mol}^{-1}$ is very close to the spin-only value of $17.65 \text{ cm}^3 \text{ K mol}^{-1}$ corresponding to eight non-interacting Co^{II} ions. Upon cooling, this value remains constant until $\sim 120 \text{ K}$, below which it decreases to reach the minimum value of $1.43 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K.

On the other hand, cluster 3 ($[\text{Co}_{10}]$) displays different behavior than the three complexes already mentioned; the room temperature $\chi_{\text{M}}T$ value of $30.51 \text{ cm}^3 \text{ K mol}^{-1}$ is larger than the expected value for ten non-interacting $S = 3/2$ ions of $18.7 \text{ cm}^3 \text{ K mol}^{-1}$ (for $g = 2$), suggesting the presence of significant orbital contribution, as has been previously reported for other $[\text{Co}^{\text{II}}_{10}]$ clusters.¹² Upon cooling the $\chi_{\text{M}}T$ value decreases rapidly to reach the minimum value of $3.12 \text{ cm}^3 \text{ K mol}^{-1}$, suggesting the presence of dominant and strong antiferromagnetic interactions.

The presence of the antiferromagnetic interactions in all complexes was further established by Curie–Weiss analysis of the high temperature (50–300 K) magnetic susceptibility data (Fig. 9), yielding negative θ values for all of them.

Complex 2 joins a small family of twenty six structurally characterized heptanuclear clusters (Table 1), in various oxidation states, while complexes 7 and 3 join a family of structurally characterized octanuclear and decanuclear cobalt clusters, respectively, in which the vast majority consists exclusively of divalent metal atoms (Tables 2 and 3).

Complexes 2, 3, 4 and 7 were also studied by alternating current ac magnetic susceptibility studies as a means of investigating potential single molecule magnetism behavior, but no out-of-phase signals were observed, thus ruling out this possibility.

Conclusions

In conclusion, we have reported the syntheses, structures and magnetic properties of seven new Co complexes stabilized by an indeno-quinoxaline based oxime ligand, LH. Following our initial results on nickel cluster chemistry, we have now found that this ligand can lead to the synthesis of cobalt clusters, as well. More importantly, the ligand adopts eight different coordination modes leading to clusters with various nuclearities.

Studies are underway for the employment of the ligand in 3d–4f and 4f chemistry, and the findings will be reported in the future.

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