A planar  decanuclear cobalt(II) coordination cluster

mariam batool

A homovalent, planar cobalt(II)-based and decanuclear coordination cluster [CoII10(OH)2(bda)6(ib)6] (**1**) has been obtained by a facile solvothermal reaction of a heterovalent pentanuclear precursor [CoII3CoIII2(Hbda)2(bda)2(ib)6], which is crucial for the synthesis of compound **1**, as it can not be obtained by simple heating of the ligands and the cobalt(II) salt in DMSO.

# Introduction

Planar cobalt coordination complexes with a nuclearity bigger than seven are rarely described in literature., Transition metal polynuclear complexes are mostly molecular oxide-bridged assemblies of metals, enclosed by organic envelope, which keeps them zero-dimensional, and inhibits from polymerizing. Apart from oxide bridges halides, pseudohalides and hydroxides have also been reported. The organic moieties in the shell with arms and functional groups bind to metal ions to form a coordination complex. Due to fascinating structural and functional applications such as electronic, optical, fluorescent, catalytic and magnetism coordination cluster species have undergone remarkable development. For the synthesis of such metal complexes, the choice of ligands as bridges or terminal functionalities with the metal ions have to be considered. Although accurate prediction of design or exact crystal structure is not yet possible however, various reaction parameters such as type of metal and ligand, metal-to-ligand molar ratio, ligand denticity, pH and temperature, counter ions and presence of solvent molecules plays critical roles in the structure formation. Solvothermal strategy for the high nuclearity inorganic complexes has recently been used extensively. This method not only affords the possibility to generate unusual structural motifs which are otherwise impossible to get *via* traditional methods but also provides a one-pot synthesis for the construction of metal- organic coordinated complexes through crystal engineering. For instance, two high nuclearity complexes i.e {Mn16} and {Mn19} were synthesized *via* solvothermal method carried out at 120 °C in methanol. It is reported that high temperature and pressure have a profound role to synthesize these coordination clusters.

A few cobalt-based coordination complexes have been reported including {Co4} molecular squares and cubanes, {Co5} square pyramid, and {Co8} systems. Disk-like hepta- {Co7}, dodeca- {Co12} and tridecanuclear {Co13} coordination clusters using cobalt as metal center and different ligands are also reported.2, , In these two structures ({Co7} & {Co13}), the core structures are related to one another, in which the central cobalt ion is surrounded by a Co6-hexagon while {Co13} is the vertex-sharing oligomer of {Co7}. To the best of our knowledge, the {Co10} disk-like core structure has not been reported yet. Recently, our group reported an horseshoe-like {Co5} coordination cluster, [CoII3CoIII2(Hbda)2(bda)2(ib)6].

Herein, we have explored that by reacting this {Co5} coordination cluster under solvothermal condition in DMSO solvent, the missing disk-like decanuclear homovalent {Co10} coordination cluster, [Co10(OH)2(bda)6(ib)6] can be obtained. Interestingly, all CoIII ions of the {Co5} precursor are reduced to CoII in the {Co10} coordination cluster. This novel {Co10} structure represents the missing link between the planar {Co7} and {Co13} structures, as shown by X-ray crystallography.



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# Materials and Methods

Compound **1** was synthesized under solvothermal conditions by using our recently reported {Co5} coordination cluster, [CoII3CoIII2(Hbda)2(bda)2(ib)6]. The {Co5} was freshly prepared following the published procedure, followed by drying under reduced pressure.14 All other starting materials were from commercial sources and used as received. Solvents were used without any further purification. The IR spectrum of compound **1** was recorded on a Nicolet Avatar 360 FTIR spectrometer (KBr pellet, ν = 4000–400 cm−1). TG/DT analyses of compound **1** was performed under a flow of dry air and a heating rate of 5 K min−1 in the temperature range 25–700 °C on a Mettler Toledo TGA/SDTA 851e instrument. The ESI-MS spectrum of compound **1** in the positive ion mode was recorded on a 4000 QTRAP mass spectrometer system, using the LC/LC-MS method with direct infusion.

# Synthesis of [CoII10(OH)2(bda)6(ib)6] (1)

Freshly prepared and vacuum dried {Co5} [CoII3CoIII2(Hbda)2(bda)2(ib)6] (0.030 g; 0.02 mmol) was dissolved in 5 mL of DMSO. The green solution was placed in a sealed autoclaveable glass vial (or a Teflon-lined stainless steel autoclave) and kept in an oven 100 °C for 120 h. The oven was then turned off allowed the vial to cool to room temperature over 4 h. Pink needle-shaped single crystals of **1**, suitable for X-Ray analysis, were obtained and washed with cold methanol, yield; 0.020 g (95 %, based on Co). **Elemental analysis**, calcd. for: Co10C72H146N6O26 (2101.28 g mol–1; no solvent): C, 41.15; H, 7.00 and N, 4.00 %. Found: C, 41.11; H, 6.96 and N 3.98 %. **MS (MeCN, ESI +)**: *m/z*: 2013.3202 (Co10C68H139N6O24+; 100 %; [CoII10(OH)2(bda)6(ib)5]+ –ib–; theoretical: 2013.3155). **IR** **(KBr pellet),** ***ν*max** **/ cm−1**: 3441 (s, br), 2960 (s), 2928 (s), 2866 (s), 1556 (s), 1477 (m), 1433 (m), 1375 (w), 1361 (w), 1290 (w), 1167 (w), 1095 (s), 1071 (m), 1043 (w), 928 (vw), 894 (m), 849 (w), 764 (vw), 596 (m), 549 (w).

Overall, compound **1** can be synthesized in three steps while only the last step is a solvothermal reaction (scheme 1). A reaction of freshly prepared cobalt(II) isobutyrate (Co(ib)2) and *N*-butyldiethanolamine (H2bda) in a molar ratio of 5:3 was carried out under similar conditions, however the reaction did not yield the final compound **1**. Likewise, a reaction of the {CoII3CoIII2} precursor was carried out in DMSO under non-solvothermal conditions and heated at 100 °C; the recrystallization of the product provided same dark green precursor {Co5}. Thus, use of the precursor complex ({Co5} = {CoII3CoIII2}) along with solvothermal method is necessary for the synthesis of compound **1**.

Scheme **1**: Three-step reaction of compound **1**.

# X-ray crystal structure analysis; TGA Literature

Complex **1** [CoII10(OH)2(bda)6(ib)6] crystallizes in the triclinic space group *P-1*. Its molecular structure (figure 1) displays a planar decanuclear cobalt(II) metal core. It consists of ten octahedrally coordinated Co(II) ions, six bda2– ligands, six ib– ligands and two OH– groups. The oxidation states of the cobalt atoms are established by bond valence sum analysis [Σbv(CoII) = 1.89 – 1.97] and they are in agreement with charge neutrality arguments of coordination cluster.

In the molecular structure six Co(II) ions are in a NO5 and four in an O6 environment. Co2, Co4, Co2´ and Co4´ are highly distorted, with one unusual long Co–Oib bond of each (Co2–O6, 2.466(3) Å and Co4–O11, 2.363(3) Å), which are about 0.3 Å longer than the other Co–Oib bonds. Co1 binds to both OH– groups, and to four *µ*4-O-atoms of four different bda2– ligands. It is connected with Co2, Co3, Co1´, Co3´, Co4´ and Co5´ through these oxo bridges. Co2 is chelated by one bda2– ligand through its N- and O-atoms. The coordination sphere of Co2 is filled by one ib– ligand and one *µ*4-O-atom of an ethoxide rest of a second bda2– ligand. Co3 is coordinated by one bda2– ligand in a chelating fashion. It binds to one OH– group (Co3–O1: 2.146(3) Å) and the coordination sphere is filled by two *µ*3-Obda-atoms of two different bda2– ligands. The coordination of Co4 is similar to this of Co2, and differs only in the bond length. Co5 binds to three isobutyrate ligands, one is chelating the Co5 atom, and to one O-atom of the remaining two. The octahedral coordination is filled by two *µ*4-Obda-atoms, which lead to an O6 coordination environment.

*Table 1*: Selected bond lengths (in Å) and angles (in °) of compound **1**.

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| --- |
| **Cobalt-ligand bonds in** **Å** |
| Co–OOH |
| Co–*µ*3-Obda |
| Co–*µ*4-Obda |
| Co–Nbda |
| Co–Oib (chelating) |
| Co–Oib (*η*1 of *µ*3-*η*1:*η*2 ib–) |
| Co–Oib (*η*2 of *µ*3-*η*1:*η*2 ib–) |
| Co···Co (neighboring) |
| Co···Co (longest) |
| Co3···Co3´ |
| **Co1-oxo-Co angles in °** |
| Co1–O–Co1´  Co1–O–Co2  Co1–O–Co3  Co1–O–Co3´  Co1–O–Co4´ |
| Co1–O–Co5´ |

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

High nuclear CoIInCoIIIm coordination clusters with planar Con+m arrays have been reported for n = 7 (m = 0); n = 9 (m = 3) and n = 11 (m = 2). To the best of our knowledge the title compound {CoII10} thus represents the largest homovalent planar Co complex with n = 10 (m = 0) (see Figure 3).

The literature known high-nuclear planar Co complexes were synthesized under various conditions using different organic ligands and Co sources. The {CoII7} complex of Pattacini *et al*. [12] was synthesized under inert gas atmosphere with anhydrous CoCl2, pyridine-2-ylmethanol (= HLig1) and NaH in THF at room temperature. [CoII7(Lig1)12]Cl2 was obtained in a yield of 35 % as orange crystals. The complex is dicationic and all oxo-bridges between the Co(II) centers belong to the used ligand. {CoII9CoIII3} was published by Zheng *et al*. in 2010 [13]. The complex was synthesized at room temperature too, but they used Co(ClO4)2∙6H2O, NaN3, 2-benzimidazolemethanole (= HLig2) and triethanolamine (H3tea) in methanol. [CoII9CoIII3O3(N3)4(Lig2)15](ClO4)2·H3tea·9.5H2O was obtained in yield of 67 % as deep-brown crystals. Although H3tea is not incorporated in the structure, it seems to be necessary for the crystallization as it is co-crystallized, the preparation of the complex under ambient conditions leads to the coordination of three discrete oxygen atoms, which are in the center of the {CoII9CoIII3} complex. [CoII11CoIII2(OH)4(piv)4(acac)6(Lig3)4(H2O)4](piv)2∙H2O (Hpiv = pivalic acid, acac– = acetylacetonate, H3Lig3 = 1,1,1-tris(hydroxymethyl)-propane [2], which was published by Leng and others, was synthesized using Co(acac)2, H3Lig3 and pivalic acid in MeOH. The solution was heated up to 120 °C for 50 h in a Teflon-lined stainless steel autoclave and the {CoII11CoIII2} complex was obtained as red crystals in a yield of 35 %. Here the waiver of the use of inert gas leads to the incorporation of discrete hydroxide groups and water molecules into the complex. In comparison the title compound was synthesized under solvothermal conditions (as {CoII11CoIII2}) without the use of inert gas, as it was done for the homovalent {Co7} complex. In this work the use of a precursor complex ({CoII3CoIII2}) was crucial, instead of using a simple Co(II) salt, to obtain [CoII10(OH)2(bda)6(ib)6] as pink crystals in yield of 95 %, which contains discrete OH—groups.

# IR and Stability (TGA and ESI-MS)

The IR spectrum of compound **1** displays asymmetric (asym.) and symmetric (sym.) stretching vibrational bands of C–H (methyl groups) between 2960 cm–1 to 2866 cm–1. The coordinated carboxylate groups (COO–) cause an asymmetric stretching vibration band at 1556 cm–1 and the corresponding symmetric stretching vibration band at 1433 cm–1. Asymmetric and symmetric deformation vibrational bands of C–H ((methyl groups) are obtained as a strong single band at 1477 cm–1 (asym.), a weak doublet at 1375 cm–1 (sym.) and 1361 cm–1 (sym.). The broad band at 3441 cm–1 is attributed to –OH (hydroxyl), along with some moisture.

The thermogravimetric analysis revealed that the compound **1** is surprisingly thermally stable up to 225 °C (see Fig. S4) when compared with {Co5} precursor (140 °C ). Compound **1** decomposes in two exothermic different sized steps in the temperature range of 225–370 °C with a total weight loss of 61.8 %. The first smaller step (225–268 °C) shows a weight loss of 15.7 %, which could be attributed to the loss of four isobutyrate ligands  (∆mcalcd. = 16.6 %) and the second step (268–370 °C) with a weight loss of 46.1 % is in good agreement with the loss of the remaining two isobutyrate ligands, one bda2– ligand, five bda2– ligands without their oxygen atoms and the two hydrogen atoms of the discrete OH groups (∆mcalcd. = 46.2 %). The thermal stability of compound **1** demonstrates that a facile reaction of the recently obtained {CoII3CoIII2} precursor complex, leads to a new coordination complex, where the physical properties are increased and optimized, by a rearrangement and extension of the molecular structure, as well as a reduction of Co(III) to Co(II) oxidation state. In addition, the stability of compound **1** was also evaluated *via* ESI-MS analysis in acetonitrile. The results showed that an 100% intensity peak is appeared at 2013.3 m/z ratio, which is attributed to Co10C68H139N6O24+ [CoII10(OH)2(bda)6(ib)5]+ theoretical *m/z*: 2013.3155 (see Fig. S1 and S2). These results further confirms the high stability of [CoII10(OH)2(bda)6(ib)6], in particular in acetonitrile .

 Which four?

 Not possible to tell, we could assume all four not chelating ib-ligands

 Please add in the TGA curve and ESI-MS graphs.

# Magnetochemical Analysis

The magnetic data of compound **1** are shown in Figure 3 as *χ*m*T* *vs.* *T* plot at 0.1 T and *M*m *vs.* *B* plot at 2.0 K. The high nuclearity of the complex precludes a detailed analysis of the magnetic data based on a microscopic model Hamiltonian. The value of *χ*m*T* at 290 K is 29.12 cm3 K mol–1, which is well within the range 23.12 – 33.81 cm3 K mol–1 expected for ten non-interacting high-spin CoII centers. With decreasing temperature, *χ*m*T* initially slowly increases down to 40 K and then more rapidly increases to reach a maximum value of 41.17 cm3 K mol–1 at 5.0 K, and finally drops off to 37.34 cm3 K mol–1 at 2.0 K. The increasing values as well as the observed maximum reveal dominant ferromagnetic exchange interactions between the ten CoII centers of **1**. The decrease of *χ*m*T* at low temperatures is most likely caused by a minor Zeeman effect due to the applied field in addition to the thermal depopulation of the energy substates rather than antiferromagnetic exchange interactions that can, however, not be excluded. These conclusions are consistent with the observed behavior of the molar magnetization at 2.0 K that increases up to 1 T (xx *N*A *µ*B) and subsequently increases to 22.1 *N*A *μ*B at 5.0 T without reaching saturation. This is about half the expected saturation value of about 45 *N*A *μ*B derived from the *χ*m*T* value at 290 K. Considering octahedral coordination geometry of high-spin CoII centers, such a value indicates either no or small exchange interactions.

H. Lueken, *Magnetochemie*, Teubner, Stuttgart, **1999**.

# Conclusion

In summary, we reported the first planar {CoII10} coordination cluster with a high thermal stability up to 225 °C, which was obtained solvothermally upon reduction of the {CoII3CoIII2} precursor in DMSO. The [CoII10(OH)2(bda)6(ib)6] complex shows predominant ferromagnetic exchange interactions.

The structural motif of the complex opens perspectives for the development of thin, planar shaped metal-oxo frameworks.

 And what else to conclude?

 What do you think?

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# Magnetic susceptibility measurements

Magnetic susceptibility data of compound **1** was recorded using a Quantum Design MPMS-5XL SQUID magnetometer for direct current (dc) and alternating current (ac) measurements. The polycrystalline samples were compacted and immobilized into cylindrical PTFE capsules. The dc susceptibility data were acquired as a function of the field (0.1–5.0 T) and temperature (2.0–290 K). The ac susceptibility data were measured in the absence of a static bias field in the 10–1000 Hz frequency range (T = 2.0–50 K, Bac = 3 G), but no out-of-phase signals were detected. Data were corrected for diamagnetic contributions from the sample holder and the compounds (χdia(**1**) = \_\_\_ cm3 mol−1).

# Acknowledgements

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