Microwave-assisted synthesis: from a mononuclear \{Co\textsuperscript{II}\} complex to \{Co\textsuperscript{II}\}_9 solvomorphs†

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We report a new \{Co\textsuperscript{II}\}_9 complex with an unprecedented structure and its solvated analogue, using microwave heating to tune the synthesis and improve the product selectivity.

Polymetallic 3d and/or 4f complexes have attracted a great deal of interest due to their interesting properties and applications in scientific fields such as molecule-based magnets, magnetic refrigerants, water oxidation electrocatalysts and MRI contrast agents.\textsuperscript{1} Therefore, the need to synthesise and characterise these complexes continues to grow. Microwave-assisted synthesis is being employed more frequently in inorganic synthesis, instead of conventional heating in an oven, due to three main advantages: reduced reaction times, increased yields and product selectivity.\textsuperscript{2} However, there are still only limited examples of polynuclear coordination complexes synthesised using this method.\textsuperscript{3,4}

We have investigated the coordination chemistry of the polydentate ligand bicine (H\textsubscript{3}bic, N,N-bis(2-hydroxyethyl) glycine)\textsuperscript{5} with Co\textsuperscript{II}. Herein, we report a new, microwave-assisted synthetic procedure for the previously reported [Co\textsuperscript{II}(H\textsubscript{2}bic)Cl] (1)\textsuperscript{6} (Fig. 1 left). Furthermore, we present a new nonanuclear complex [Co\textsuperscript{II}\textsubscript{9}(Hbic)\textsubscript{4}(bic)\textsubscript{2}Cl\textsubscript{4}] (2), with an unprecedented metallic core (Fig. 1 right), and its solvated analogue [Co\textsuperscript{II}\textsubscript{9}(Hbic)\textsubscript{4}(bic)\textsubscript{2}Cl\textsubscript{4}]·12H\textsubscript{2}O (2·12H\textsubscript{2}O), by adjusting the synthetic procedure used for 1. The reaction of CoCl\textsubscript{2}·6H\textsubscript{2}O with bicine and NEt\textsubscript{3} in EtOH under solvothermal conditions, resulted in a mixture of the complexes 1 (pink block-like crystals), 2 (blue block-like crystals) and 2·12H\textsubscript{2}O (blue needle-like crystals). However, by using microwave-assisted heating the selectivity is improved (see Scheme 1) and 1, 2 and 2·12H\textsubscript{2}O can be isolated separately. The full experimental procedure is included in the ESI.†

Complex 1 crystallises in the orthorhombic \textit{Pbca} space group,\textsuperscript{6} while single-crystal X-ray diffraction for 2 and 2·12H\textsubscript{2}O revealed that the complexes crystallise in the monoclinic \textit{P2}_{1}/\textit{n}

![Fig. 1 The molecular structure of 1 (left) and \{Co\textsuperscript{II}\}_9(Hbic)\textsubscript{4}(bic)\textsubscript{2}Cl\textsubscript{4}](right). Colour code: Co\textsuperscript{II}: violet, Cl: green, O: red, N: blue, C: grey. Hydrogen atoms are omitted for clarity.](image)

Scheme 1  The synthetic procedure followed to isolate complexes 1, 2 and 2·12H\textsubscript{2}O.

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and trigonal $R_3$ space groups, respectively. The crystallographic
data for 2 and 2-12H$_2$O can be found in Table S1 (see ESI†).
The Co$^{II}$ centre in complex 1 is five-coordinate and adopts a
distorted trigonal bipyramidal (TBP) geometry, with one singly
deprotonated bicine ligand and one terminal Cl$^-$ ligand.
Continuous shape measures (CShMs),\textsuperscript{7} which provide an
estimate of the distortion from the ideal TBP geometry for the
Co$^{II}$, give a value of 1.42 (where 0 corresponds to the ideal poly-
hedron), confirming a significant distortion (Table S2 and
Fig. S1, ESI†). Bond Valence Sum (BVS) analysis was used to
confirm the oxidation state of Co$^{II}$.\textsuperscript{8} Intermolecular hydrogen
bonds occur between the hydroxyl groups and the carboxylate
groups of neighbouring molecules, forming a two-dimensional
network (Fig. S2, ESI†). The shortest intermolecular Co··Co`
distances are \textasciitilde 4.8 \textup{Å}.\textsuperscript{6}

The new nonanuclear complex 2 adopts an unprecedented
structural motif which consists of a \{Co$^{II}\}$ disk-like core with
two additional tetrahedral Co$^{II}$ centres. There are only a few examples of \{Co$^{II}\}$ complexes and none of them adopt a
similar topology as the complex presented here.\textsuperscript{9,10} The crystal
packing of 2 and 2-12H$_2$O is different (Fig. 2) due to the co-
crystallised molecules of water. Small differences are observed in
the distortion of the geometries of the cobalt centres and
CShMs values for all Co$^{III}$ centres for 2 and 2-12H$_2$O were calcu-
lated with the programme SHAPE\textsuperscript{11} (Tables S3 and S4, ESI†).
Seven Co$^{III}$ centres adopt distorted octahedral geometries, while
the remaining two adopt slightly distorted tetrahedral

geometries. All nine cobalt centres in 2 are in the +2 oxidation
state, as confirmed by BVS analysis.\textsuperscript{5} Five Co$^{III}$ (Co1, Co2, Co2',
Co3, Co3') centres define a plane while Co4, Co4', Co5 and
Co5' are located outside this plane (Fig. S3†). This puckered
\{Co$^{III}\}$ motif is also found in \{Co$^{III}\}$ with similar donor atoms
and is not likely to be a result of the extra Co5/Co5' centres.\textsuperscript{12}
Intramolecular interactions are present between the hydroxyl
and carboxylate groups of 2 and 2-12H$_2$O. In the solvomorph
2-12H$_2$O intermolecular interactions occur between the
hydroxyl and carboxylate groups of neighbouring molecules
with the molecules of solvent (see Fig. S4†).

In order to examine if it is possible to isolate the three com-
pounds separately we investigated further by making various
changes to the synthetic procedure (e.g. the amount of base,
the cobalt salt, the reaction time and/or temperature used in
the solvothermal reactions). However, solvothermal conditions
always led to a mixture of crystals or crystalline precipitates;
therefore, we investigated microwave heating instead. Under
microwave heating, in EtOH with a ligand to base ratio \textasciitilde 4:1 a
pink crystalline powder is isolated, whereas when the ligand to
base ratio is changed to 1:1, a blue crystalline powder is
formed (for full experimental description see ESI†). Both pro-
ducts were collected by filtration and dried in air, and powder
X-ray diffraction (Fig. 3) revealed that the pink and blue pro-
ducts corresponded to complexes 1 and 2-12H$_2$O, respectively.
Moreover, when the blue crystalline product is instead col-
clected by filtration and dried under a nitrogen atmosphere,
complex 2 is obtained, as confirmed by powder X-ray diffraction
(Fig. 3). Hence, the \{Co$^{III}\}$ crystal packing (Fig. 2) depends on
the drying process (Scheme 1) i.e. drying under an inert
atmosphere (glove bag) gives 2, whereas drying in air gives
2-12H$_2$O. Therefore, depending on which drying process is
applied, we are able to control which \{Co$^{III}\$ solvomorph is
formed.

Variable temperature dc susceptibility data were collected
for 1, 2 and 2-12H$_2$O in a field of 1000 Oe in the 290–2 K tem-
perature range (Fig. 4 and 5). At 290 K the $\chi_M T$ value of 1 is
2.57 cm$^3$ mol$^{-1}$ K, higher than the expected $\chi_M T = 1.88$ cm$^3$
 mol$^{-1}$ K for a high-spin Co$^{III}$ ($S = 3/2$ and $g = 2$), indicating a
spin–orbit coupling contribution. Upon cooling, $\chi_M T$ decreases
slowly until \textasciitilde 12 K, then increases slightly at 8 K (2.27 cm$^3$
 mol$^{-1}$ K) and drops again to a minimum at 2 K. This behav-


ior indicates the presence of magnetic anisotropy and weak
ferromagnetic intermolecular interactions\textsuperscript{13} (hydrogen bonds
are present and the Co$^{III}$ centres of neighbouring molecules in
1 are close \textasciitilde 4.8 \textup{Å}, although we were unable to obtain a satis-
factory ferromagnetic $g$ term when included in the fit. Magnetisation versus field plots at 2, 4 and 6 K did not satu-
rate, a further indication of the presence of magnetic an-
isotropy (Fig. 4 inset). The dc magnetic susceptibility data and
the magnetisation curves of 1 were fitted simultaneously using
the programme PHI\textsuperscript{14} (Fig. 4). Attempts to fit the data with an
anisotropic $g$ value were not successful, while using a positive
$D$ did not produce reasonable results, which is a strong indi-
cation that an easy-axis magnetic anisotropy is present here.
This assumption is reasonable, since the use of a tripodal

Fig. 2 The crystal packing of 2 (top) and 2-12H$_2$O (bottom) along
the crystallographic c-axis. The water molecules inside the channels
of 2-12H$_2$O are omitted for clarity. Colour code: Co$^{III}$: violet, Cl: green, O:
red, N: blue, C: grey. Hydrogen atoms are omitted for clarity.
ligand can enforce $C_3$ symmetry and, as has been seen in previously reported examples, an easy-axis anisotropy ($D < 0$) can be promoted. The extracted parameters from the fitting of the data are: $g = 2.25$, $D = -5.92$ ($\pm 0.24$) cm$^{-1}$ and $E = -1.32$ ($\pm 0.09$) cm$^{-1}$, with $\chi_{\text{TP}} = 0.0006$ cm$^3$ mol$^{-1}$ for a Co$^{II}$ in TBP geometry.$^{16}$

The $\chi_M T$ values at room temperature for 2 and 2·12H$_2$O are 23.4 and 23.8 cm$^3$ mol$^{-1}$ K, respectively, which are higher than the theoretical spin-only value $\chi_M T = 16.9$ cm$^3$ mol$^{-1}$ K for nine non-interacting high-spin Co$^{II}$ ($S = 3/2$ and $g = 2$), indicating a spin–orbit coupling contribution. $\chi_M T$ slowly decreases with the decrease of temperature until 26 and 19 K for 2 and 2·12H$_2$O, due to the presence of spin–orbit coupling; then $\chi_M T$ increases sharply at 6 K for both complexes reaching the values of 26.2 and 21.5 cm$^3$ mol$^{-1}$ K for 2 and 2·12H$_2$O respectively, which can be attributed to the presence of ferromagnetic exchange interactions. Finally, $\chi_M T$ decreases for both complexes at low temperature, due to zero-field splitting (ZFS) and/or intermolecular antiferromagnetic interactions.

Magnetisation versus field plots at 2, 4 and 6 K did not saturate for both complexes, an indication of the presence of magnetic anisotropy (Fig. S5†). This behaviour is in agreement with other polynuclear Co$^{II}$-based complexes.$^{4,10,17}$ It was not possible to fit the data due to the complexity of the system and the presence of octahedral Co(II).

Ac susceptibility measurements were performed for all complexes in order to examine if there is slow relaxation of the magnetisation. Complex 1 does not display any out-of-phase ac signal in zero or an applied dc field. This could be attributed to the significant distortion of the TBP geometry around Co$^{II}$, the presence of hydrogen bonds between neighbouring molecules and/or the short intermolecular Co···Co distances ($\sim 4.8$ Å). Complex 2 displays only the onset of out-of-phase signals in zero or an applied 2000 Oe dc field (Fig. S6†), while complex 2·12H$_2$O does not display any out-of-phase signals in zero or an applied dc field (Fig. S7, ESI†). The different behaviour between the two {Co$^{II}$} complexes could be ascribed to the subtle structural differences between the two complexes (slightly different distortion of the Co$^{II}$ centres, Tables S3 and S4, ESI†) and/or the absence of solvent molecules in the crystal lattice of 2. It has been previously reported that the absence or change of solvent can drastically affect the magnetic properties of a complex.$^{18}$

In conclusion, we report a new {Co$^{II}$} complex [Co$_5^{II}$Hbic$_4$(bic)$_2$Cl$_4$] (2), which extends the well-known {Co$^{II}$}
and its solvomorph $[\text{Co}^\text{II}(\text{Hbic})_4(\text{bic})_2\text{Cl}_4] \cdot 12\text{H}_2\text{O}$ (1) \cite{4} In particular, this work highlights the potential of microwave-assisted synthesis in the synthesis of polymeric complexes using polydentate ligands where bench or solvothermal synthesis leads to a mixture of products. We believe that this approach will prove applicable to a wide range of systems.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**


