



## 2-Amino-2-methyl-1,3-propanediol (ampdH<sub>2</sub>) as ligand backbone for the synthesis of cobalt complexes: Mononuclear Co(II), binuclear Co(II,III) and hexanuclear Co(II,III)

Tannistha Roy Barman<sup>a</sup>, Manas Sutradhar<sup>a,\*</sup>, Michael G.B. Drew<sup>b</sup>, Eva Rentschler<sup>a,\*</sup>

<sup>a</sup>Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University of Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany

<sup>b</sup>School of Chemistry, The University of Reading, P.O. Box 224, Whiteknights, Reading RG6 6AD, UK

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### ABSTRACT

Three cobalt complexes have been synthesized using 2-amino-2-methyl-1,3-propanediol (ampdH<sub>2</sub>) and its Schiff base derivative ligands and structurally characterized. The three complexes **1**, **2** and **3** are very different and consist of mononuclear Co(II), mixed-valence binuclear Co(II,III) and mixed-valence hexanuclear Co(II,III) complexes respectively. The properties of the coordinated donor atoms of the ligand play the predominant role in stabilizing the oxidation states of the cobalt centers. The presence of intermolecular hydrogen bonds in **1** via non-coordinating perchlorate ions lead to the formation of a 1D-chain network while a sheet-like 2D network was observed in **3**.

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### 1. Introduction

Since the discovery of the first example of a single molecule magnet, SMM [**1**], a mixed-valence [Mn12] compound, in 1993, special emphasis has been placed on the synthesis of mixed-valence multinuclear cluster compounds and in studying their magnetic properties. A large number of mixed-valence transition metal clusters have been synthesized and their magnetic properties have been thoroughly investigated [2–6]. Beside the interesting magnetic properties such as single-molecular magnet and single-chain magnet [7–11], catalytic properties [12–16] have also been explored. In comparison with the rich cluster chemistry generated by manganese, iron and vanadium in various oxidation states, the number of hydroxo- and/or alkoxo-bridged cobalt clusters is more limited [17–29]. In the field of SMMs, cobalt(II) complexes are at early stage of development in comparison to other metal ions and the first cobalt-based SMM, reported by Yang et al. in 2002, was a metal-oxo cubane [30]. The magnetic behaviour of SMMs results from the combination of a large ground spin state (*S*) with a large and negative *l*<sub>S</sub> (or easy-axis) type of magnetoanisotropy, as measured by the axial zero-field splitting parameter *D* [9–11,31]. Since cobalt(III) is diamagnetic, the interesting magnetic properties of mixed-valence cobalt clusters arise from cobalt(II), which is a paramagnetic ion with a large single-ion anisotropy (or strong Ising-type anisotropy)

\* Corresponding authors.

E-mail addresses: [manaschem@yahoo.co.in](mailto:manaschem@yahoo.co.in) (M. Sutradhar), [rentschl@uni-mainz.de](mailto:rentschl@uni-mainz.de) (E. Rentschler).

due to the orbitally degenerate ground state and therefore may be a good candidate for making SMMs. But, in only a few cases has SMM behaviour been observed [32–36]. In the present study, we have synthesized various mixed valence Co(II,III) complexes using an amino polyalcohol as a ligand backbone which was selected because it and its Schiff base derivatives are versatile ligands in terms of donor properties and so are able to form higher nuclearity compounds. Herein we report, the syntheses and structural characterization of a mononuclear Co(II) complex [Co<sup>II</sup>(L<sup>1</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**), a binuclear mixed-valent Co(II,III) complex [Co<sup>III</sup>Co<sup>II</sup>(L<sup>2</sup>)(H<sub>2</sub>O)(OCH<sub>3</sub>)]ClO<sub>4</sub>(**2**)-2CH<sub>3</sub>OH and a hexanuclear mixed-valent Co(II,III) complex [Co<sup>III</sup><sub>2</sub>Co<sup>II</sup><sub>4</sub>(piv)<sub>6</sub>(ampd)<sub>4</sub>](**3**)-3.5CH<sub>3</sub>CN·2H<sub>2</sub>O using two different Schiff bases L<sup>1</sup> and H<sub>2</sub>L<sup>2</sup> derived from 2-amino-2-methyl-1,3-propanediol(ampH<sub>2</sub>).

### 2. Experimental

#### 2.1. Materials

[Co<sub>2</sub>(μ-OH<sub>2</sub>)(μ-Piv)<sub>2</sub>(Piv)<sub>2</sub>(HPiv)<sub>4</sub>], Piv = trimethylacetate, was prepared following a previously reported procedure [37]. All other chemicals were reagent grade and used as received without further purification.

#### 2.2. Physical measurements

Elemental analyses (C, H and N) were performed with a Foss Heraeus Vario EL elemental analyzer. Molecular weights and

formulas were calculated without solvent molecules unless explicitly stated. Infrared spectra were recorded in the 400–4000  $\text{cm}^{-1}$  range with a Jasco FT/IR-4200 spectrometer. The measurements were carried out by using the pellet technique with KBr as embedding medium.

### 2.3. X-ray crystallographic data collection and refinement of the structures

Single crystals of **1**, **2** and **3** were coated with perfluoropolyether, picked up with a glass fiber, and mounted on a SMART APEX II CCD diffractometer equipped with a nitrogen cold stream operating at 173(2) K. Graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) from a fine-focus sealed tube was used throughout. Cell constants were obtained from a least-square fit of the diffraction angles of several thousand strong reflections. Data reduction was carried out with APEX2 v2.0 [38], while SIR-97 [39] and SHELXL-97 [40] were used for the structure solution and for the refinement, respectively. Hydrogen atoms bonded to carbon and nitrogen were given ideal positions, while those bonded to oxygen were located in difference Fourier maps and refined with distance constraints, though those in the water molecules in **3** could not be located. Hydrogen atoms were given thermal parameters equal to 1.2 times those of the atoms to which they were bonded apart from those in methyl groups or bonded to oxygen for which the factor was 1.5. **2** was chiral with a Flack parameter refined to 0.013(17). Absorption corrections were done by semi-empirical routine MULTISCAN implemented in the PLATON crystallographic software package. Further details of crystal data and refinement are given in Table 1.

### 2.4. Synthesis

#### 2.4.1. Synthesis of the ligands

Three ligands are used in this work as shown in Scheme 1. Two Schiff base ligands,  $L^1$  and  $H_2L^2$  were prepared by refluxing the 2-amino-2-methyl-1,3-propanediol ( $\text{ampdH}_2$ ) (10 mmol) with pyridine-2-carboxaldehyde (10 mmol) and salicylaldehyde (10 mmol) in methanol solution (20  $\text{cm}^3$ ) respectively for ca. 2 h. The ligands were not isolated. The methanol solutions were used for the syntheses of the complexes.

**Caution!** Perchlorate salts are potentially explosive could detonate upon heating. This complex should be handled with care and only in small amounts.

#### 2.4.2. Synthesis of $[\text{Co}^{\text{II}}(L^1)_2](\text{ClO}_4)_2$ (**1**)

To a methanolic solution (20  $\text{cm}^3$ ) of cobalt(II) perchlorate hexahydrate (5 mmol, 1.83 g), methanol solution (10 mmol) of the ligand  $L^1$  was added and refluxed for 1 h. The color of the mixture turned pink-red. The solution was filtered and kept at room temperature for crystallization. After 2–3 days reddish pink single crystals were isolated, washed 3 times with cold methanol and dried in open air. Yield: 68%. *Anal. Calc.* for  $\text{C}_{20}\text{H}_{28}\text{N}_4\text{O}_{12}\text{Cl}_2\text{Co}$ : C, 37.17; H, 4.37; N, 8.67. Found: C, 37.11; H, 4.42; N, 8.61%. IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3454, 3216 (OH), 1626 (C=N), 1248 (N–N).

#### 2.4.3. Synthesis of $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(L^2)(\text{H}_2\text{O})(\text{OCH}_3)]\text{ClO}_4 \cdot 2\text{CH}_3\text{OH}$

To a methanolic solution (20  $\text{cm}^3$ ) of cobalt(II) perchlorate hexahydrate (5 mmol, 1.83 g), methanol solution (10 mmol) of the ligand  $H_2L^2$  was added and refluxed for 1 h. The color of the mixture turned pink-red. The solution was filtered and kept at room temperature for crystallization. After 2–3 days reddish pink single crystals were isolated, washed 3 times with cold methanol and dried in open air. Yield: 71%. *Anal. Calc.* for  $\text{C}_{23}\text{H}_{31}\text{N}_2\text{O}_{12}\text{ClCo}_2$ : C, 40.58; H, 4.59; N, 4.11. Found: C, 40.49; H, 4.52; N, 4.07%. IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3384 (OH), 1608 (C=N), 1249 (N–N).

#### 2.4.4. Synthesis of $[\text{Co}^{\text{III}}_2\text{Co}^{\text{II}}_4(\text{piv})_6(\text{ampd})_4]$ (**3**) $\cdot 3.5\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$

To an acetonitrile solution (50 ml) of  $[\text{Co}_2(\mu\text{-OH}_2)(\mu\text{-Piv})_2(\text{Piv})_2(\text{-HPiv})_4]$  (2.5 mmol, 2.37 g) solid  $\text{ampdH}_2$  (5 mmol, 0.53 g) was added and stirred at room temperature for 1 h. The violet color of the solution turned pink. The solution was filtered and kept at room temperature for crystallization. After 2–3 days reddish violet single crystals were isolated, washed 3 times with cold acetonitrile solution and dried in open air. Yield: 64%. *Anal. Calc.* for  $\text{C}_{46}\text{H}_{90}\text{N}_4\text{O}_{20}\text{Co}_6$ : C, 40.25; H, 6.61; N, 4.08. Found: C, 40.19; H, 6.53; N, 4.11%. IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3468 (OH), 1586 (COO)<sub>as</sub>, 1488 (COO)<sub>s</sub>.

**Table 1**

Crystal data and structure determination summary of complexes **1**, **2** and **3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$\text{C}_{20}\text{H}_{28}\text{N}_4\text{O}_{12}\text{Cl}_2\text{Co}$	$\text{C}_{25}\text{H}_{40}\text{N}_2\text{O}_{14}\text{ClCo}_2$	$\text{C}_{52.5}\text{H}_{104.25}\text{N}_{7.25}\text{O}_{22.25}\text{Co}_6$
Formula weight	646.29	745.90	1546.76
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1$	$P\bar{1}$
<i>a</i> (Å)	9.5772(7)	9.786(5)	14.0143(13)
<i>b</i> (Å)	37.473(2)	14.168(5)	16.2375(15)
<i>c</i> (Å)	7.9351(5)	11.278(5)	16.8650(16)
$\alpha$ (°)	(90)	(90)	110.486(2)
$\beta$ (°)	112.827(2)	101.888(5)	98.244(3)
$\gamma$ (°)	(90)	(90)	90.775(3)
<i>V</i> (Å <sup>3</sup> )	2624.8(3)	1530.1(12)	3549.5(6)
<i>Z</i>	4	2	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.635	1.619	1.447
Absorption coefficient ( $\mu$ ) mm <sup>-1</sup>	0.927	1.242	1.442
Data/restraints/param	6324/2/362	7250/9/416	16858/2/837
No. obsd reflens [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4916	5775	7345
<i>R</i> ( <i>F</i> ), <i>wR</i> ( <i>F</i> ) (obsd data) <sup>a</sup>	0.0471, 0.0937	0.0467, 0.1149	0.0527, 0.0832
<i>R</i> ( <i>F</i> <sup>2</sup> ), <i>wR</i> ( <i>F</i> <sup>2</sup> ) (all data) <sup>b</sup>	0.0699, 0.1016	0.0589, 0.1218	0.1495, 0.1008
<i>R</i> <sub>int</sub>	0.0456	0.0644	0.1253
Peaks in final difference map (e Å <sup>-3</sup> )	0.523 and -0.398	1.995 and -0.975	0.835 and -0.622
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.046	1.118	0.765

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $wR(F^2) = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4]^{1/2}$ .

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